# A KINETIC STUDY OF THE HYDROCHLORINATION OF NATURAL RUBBER AND SYNTHETIC POLYISOPRENE LATICES

BY

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## LIST OF PUBLICATIONS

The majority of the work reported in this thesis is recorded in the publications listed here.

"Ideal Copolymers and the Second Order Transitions of Synthetic Rubbers. I. Non-Crystalling Copolymers."
Gordon, M., & Taylor, J.S., J.Appl. Chem., 2, 493, (1952)

"Introduction to the Mechanism of the Hydrochlorination of Rubber."
Gordon, M., & Taylor, J.S., J.Appl. Chem., 3, 537, (1953)

"Kinetics and Mechanism of Hydrochlorination of Synthetic and Natural Polyisoprene Latex."
Crampsey, E., Gordon, M., & Taylor, J.S., J.Chem.Soc., p.3925, (1953)

"Studies in Latex Particle Surface Reactions: Kinetics of Hydrochlorination of Unvulcanized and Vulcanized Latices."
Gordon, M., & Taylor, J.S., 3rd Rubber Tech.Conf., London, (June, 1954), (in press).

## Summary of the Contribution of this Thesis

The kinetics of the hydrochlorination of natural and synthetic polyisoprene are studied in order to amplify the very limited information previously recorded in the literature regarding the nature of the reaction. The polymers are reacted in a latex process, and the accumulation of precision measurements permits a much clearer understanding of the mechanism, rate control, and loci of the reaction.

The reaction progress is followed kinetically by the use of a convenient density-gradient technique for measuring accurately the increase in density of the polymer during its hydrochlorination. Extent of reaction (% hydrochlorination) is evaluated from the den--sity change by means of a calibration provided by semi--micro potentiometric titration chlorine analyses.

A chain mechanism is postulated for the hydrochlorination of Hevea rubber latex on the basis of Bunn and Garner's accepted X-ray structure of rubber hydrochloride crystals (1). This mechanism proposes the coiling of a rubber chain segment into a trans-decalin-shaped transition state which is necessary and sufficient to explain the alternation along the rubber hydrochloride polymer chain of D- and L- asymmetric carbon atoms each separated from the next by three $CH_2$ groups.

It is proved that the hydrochlorination of polyisoprene latices occurs at two different reaction loci. The main reaction takes place within the bulk of the polymer particles. Initially superimposed on this however, there is a reaction at the interphase between the particle surface and the aqueous acid. The two reaction loci react at different rates and by different mechanisms.

Despite the fact that natural and synthetic polyisoprenes have different detailed chemical structures, practically identical zero-order rate constants applyto both substrates for the main (unretarded) hydrochlorination.. It follows that the substrates themselves do not participate in the rate control, since the rate of chain reactions which might give zero-order constants are very sensitive to detailed polymer structure. Energetic and concentration factors support the deduction that the rate is controlled by a purely inorganic step involving the formation of an ion pair ($H^+$,$Cl^-$) from solvated precursors in the rubber medium ($H_2Cl^+ + Cl^-$).

The surface reaction affects only the isoprene units lying within $15 \pm 2.5$ Å of the particle surface, i.e. about 2.5% of the rubber in Hevea latex and up to over 20% in synthetic polyisoprene latex of sufficiently small particle size. The increased extent of surface hydrochlorination in the synthetic substrate

permits kinetic measurements on it. The surface effect can be isolated at low pressures of hydrogen chloride at which the bulk rate becomes negligible. The high order surface reaction rate is controlled by the diffusion into the polymer of a reactive hydrogen chloride species of very limited stability in rubber.

The retarded zero-order bulk reaction, evident only in Hevea latex hydrochlorination, is proved to be due to the presence of a basic retarder in trace amounts within the rubber particles.

Although 100% hydrochlorination of synthetic polyisoprene latex is possible, the reaction with Hevea rubber latex comes to a standstill well before stoichiometric completion - a fact probably primarily due to the onset of crystallinity in natural rubber hydrochloride.

The influence, on both the surface and the bulk hydrochlorination rates, of prior sulphur vulcanization of synthetic polyisoprene latex is examined. The resulting rate curves suggest that vulcanization itself has a surface locus also.

The reaction kinetics are shown to be reproducible and free from uncontrolled effects despite the complexity of the latex medium ( especially Hevea latex).

# CHAPTER 1

## Introduction

### 1.1. Commercial Development of Rubber Hydrochloride

The reaction between hydrogen chloride and rubber consists in the progressive conversion of the individual unsaturated isoprene units to their hydrochlorinated form;

$$-CH_2-C(CH_3) = CH-CH_2- \longrightarrow -CH_2-\underset{Cl}{C}(CH_3)-CH_2-C\ H_2-$$

The reaction was first reported in 1900 by Weber (2), but it was not until 1934 that the addition of hydrogen chloride to rubber excited commercial interest. In that year the Goodyear Rubber Co. manufactured Pliofilm, a cellophane type of film, from rubber hydrochloride (3). Since then, the industrial production and uses of the polymer have been the subject of a number of patents.

Rubber hydrochloride is a white powdery substance of empirical formula approximately $C_5H_9Cl$. The theoretical chlorine content is 33.94%. It is highly crystalline even at room temperature. It can be drawn out to several times its own length (the crystals becoming oriented) and remains extended on release. The extensibility becomes reversible near the melting point - a property typical of crystalline polymers (4). Rubber hydrochloride is predominantly processed into transparent,

thermoplastic films whose properties of excellent water and gas impermeability, good flexibility, and high mechanical strength make it suitable as a packaging material - its main use.

Rather poor stability to light and heat, and to some extent its relatively low melting point (115°C), has hindered commercial development of the fibre-forming properties of rubber hydrochloride. Its instability to light may be traced to the difficulty in attaining complete saturation of the double bonds in the polymer. Stability to heat can be improved by the incorporation of basic stabilizers, e.g. hexamethylene tetramine or certain metallic oxides. Butyl stearate is the most common plasticizer for the polymer.

Until 1947 (5) the polymer was prepared industrially by passing hydrogen chloride gas through solutions of masticated rubber, or by treating small cubes or sheets of rubber with gaseous or liquefied hydrogen chloride under pressure. Balata and gutta percha may be hydrochlorinated also, but the products are amorphous.

## 1.2. Discovery and Experimental Advantages of Stable Acid Latex

Rubber latex is normally stable only in a basic medium, and when it is acidified the original negative charge on the rubber particles is discharged by reaction with $H^+$ and coagulation occurs. Belgrave (6) demonstrated that the sign of the charge can, infact, be reversed by acidification, but the

latex is then both mechanically and chemically unstable. The preparation of a stable acid latex by the addition of a cationic soap previous to acidification was discovered by Blow (7). Hassels reported (8) that non-ionic emulsifying agents can also be used for this preparation.

First use of this discovery was made by van Veersen (9) in 1947 when he used acidified latex itself as the medium in which to carry out the hydrochlorination of rubber. The emulsion of rubber was smoothly converted to an emulsion of rubber hydrochloride. Similar processes have been used for the cyclization of rubber by the action of sulphuric acid (10) (11) (12), and for the chlorination of rubber by gaseous chlorine (13) (14).

Since it provides a method for better control and experimentation, the acid latex technique has promoted studies on rubber reactions. More specifically, accurate kinetic measurements are made possible by its use. The advantages of studying rubber reactions in latex are equivalent to those gained when polymerizations are studied in emulsion rather than in bulk or solution. Moreover, no oxidative degradation is suffered by the rubber such as it under goes when it is coagulated, washed, and milled prior to going into solution.

## 1.3. Previous Work on Polyisoprene Hydrochlorides

From their study of polyisoprene hydrochlorides prepared from solution, Gehmann et al.(4) reported that, although balata and gutta percha hydrochlorides are amorphous, rubber hydrochloride is crystalline. They also producedevidence that cyclization in a side reaction is responsible for the incomplete saturation of the rubber.

Bunn and Garner's (1) X-ray diffraction examination of the rubber hydrochloride crystal structure revealed that the unit cell is monoclinic (pseudo orthorombic). They confirmed that the chain form is consistent with chemical addition of hydrogen chloride according to the Markownikoff rule, and further, that the $-(CH_2)_3-CMeCl-$ groups in the crystal micelle are alternately right- and left- handed. They attributed the crystallinity of the polymer to this regular structure, and suggested that the amorphous nature of balata hydrochloride may be due to the fact that, owing to the different chain structure of balata (the trans isomer of rubber), right- and left- handed groupings can only be formed indiscriminantly.

Synthetic polyisoprene hydrochloride was found to be amorphous by D'Ianni and coworkers (15).

Working with the substrate in solution, D'Ianni (16) could only attain 83 Mole.% hydrochlorination, and this he attributed to the unreactive nature of side vinyl groups formed from 1:2- addition in the polyisoprene.

It was shown by van Veersen (17) that the rate of hydrochlorination of natural rubber in solution is dependent on the solubility of hydrogen chloride in the solvent. He claimed that by hydrochlorinating rubber in latex, the extent of conversion could be raised from 90-95%, attainable in solution, to 98-99%. He ascribed the difference to the elimination of side reactions (e.g. cyclization). The rate of latex hydrochlorination was shown to increase with pressure and decrease with temperature. He tentatively suggested, without sufficient evidence, that the relatively slow rate of latex hydrochlorination under normal conditions is due to the rate being controlled by diffusion of the hydrogen chloride into the rubber. The product from latex hydrochlorination was reported to be crystalline also.

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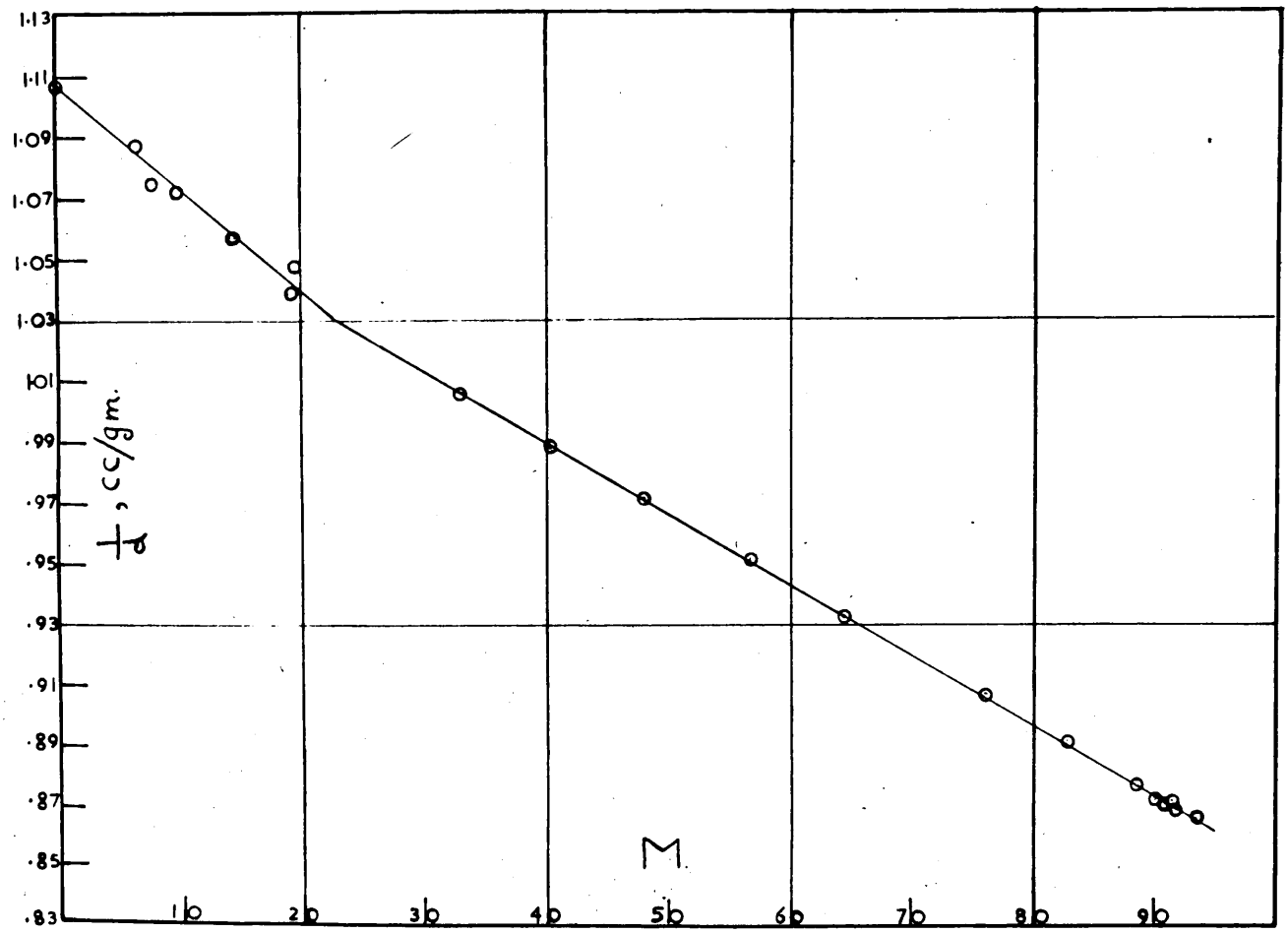
## CHAPTER 2

## The Relationship between Specific Volume and Per Cent Conversion of Partially Hydrochlorinated Hevea Rubber

In order to follow accurately the kinetic progress of the reaction between hydrogen chloride and rubber latex, a very great number of samples were required for analysis. The time factor involved prohibited the direct analysis of chlorine content of each polymer sample, and it was therefore necessary to employ a more convenient method of determining the extent of the reaction.

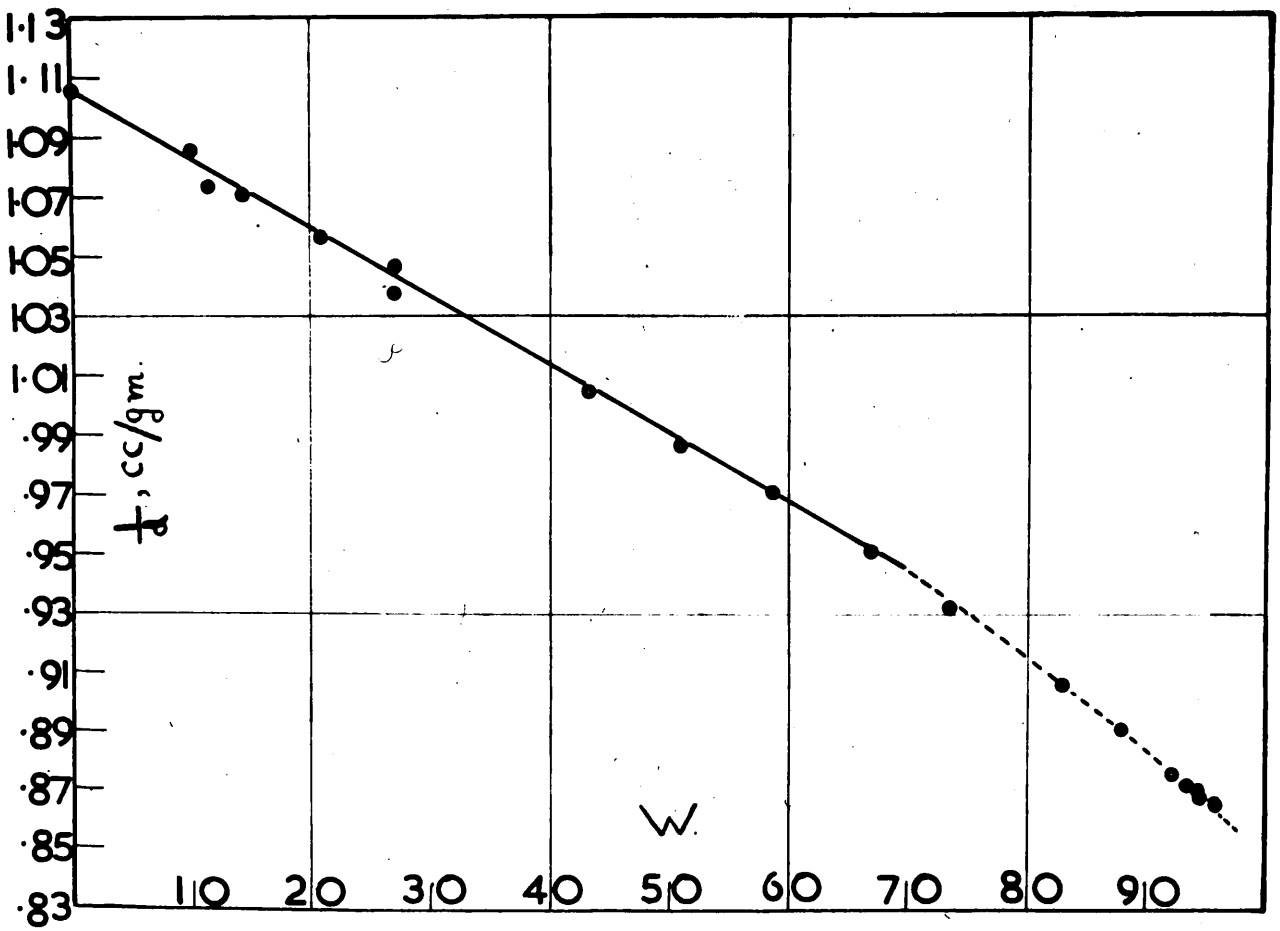
Such a method is provided by the measurement of the polymer density. The density of the polymer increases as hydrogen chloride is added across the double bonds of rubber, and the total density change for full hydrochlorination is 30% of the density of rubber. A density-gradient tube technique was used successfully by Gordon in his study of rubber cyclization (12) where a much smaller density range existed. Preliminary experiments showed that this technique could be applied to rubber hydrochlorination studies for an accurate estimation of the percentage hydrochlorination of a polymer sample.

A calibration of density against per cent




SPECIFIC VOLUME $v$, AT 26.7°C AGAINST MOLE. PER CENT HYDROCHLORINATION, M.

FIG. 1




SPECIFIC VOLUME $\frac{1}{d}$, AT 26·7°C AGAINST WT. PER CENT HYDROCHLORINATION, W.

FIG 2

(DOTTED PORTION SHOWS DOWNWARD DISPLACEMENT CAUSED BY CRYSTALLINITY.)

hydrochlorination was required. To obtain this, Hevea latex was hydrochlorinated and the samples which were withdrawn after various time intervals were, in the manner fully described later, flocculated, purified, and dried. The density and chlorine content of each was then determined. Results of those samples analyzed were used to construct the calibration curves of specific volume (reciprocal density) versus mole.% and weight % hydrochlorination illustrated in Figures 1 and 2. The relevant data for these analyses are given in Table 1 in the appendix.

Gordon and Taylor have shown that weight % conversion is the significant variable for packing studies (18), and the theoretical significance of Figure 2 will be discussed later (chapter 8.3) when the relevant plot for synthetic polyisoprene is also considered. Meanwhile, it will suffice to say that mole.% conversion figures are required for kinetic rate curves, and although Figure 1 has no theoretical significance it was convenient for estimating the mole.% hydrochlorination of unanalyzed samples by interpolation, since it happens to consist of two linear portions (meeting at a kink).

The per cent conversions for Figures 1 and 2 were calculated from the chlorine analyses by applying the following equations:

$$C = \frac{M \times 35.457 \times 100}{104.58M + (100-M)68.115} \qquad \text{(Eq.1)}$$

$$\therefore M = \frac{186.8C}{97.2 - C} \qquad \text{(Eq.2.)}$$

and

$$W = \frac{M \times 104.58 \times 100}{104.58M + (100-M)68.115} \qquad \text{(Eq.3)}$$

$$\therefore W = \frac{C \times 104.58}{35.457} \qquad \text{(Eq.4)}$$

where C is Wt.% chlorine in polymer
M is Mole.% hydrochlorination of polymer
W is Wt.% hydrochlorination of polymer

and Cl = 35.457, $C_5H_8$ = 68.115,

$C_5H_9Cl$ = 104.580

These formulae are based on the assumption that the purified polymers analyzed for chlorine were free from contamination.

Nitrogen analyses proved that the final hydrochlorination product contained protein, one of the original latex constituents, in an amount less than 0.05%. The standard micro-Kjeldahl technique was used to convert the nitrogen in the polymer into ammonium sulphate, and to distil over ammonia. To the distillate was added 1 ml. of Nessler's reagent and the volume was made up to 50 ml. with ammonia-free water. The nitrogen was

estimated colorimetrically using a photo-electric colorimeter which had been previously calibrated with standard $NH_4Cl$ solutions. A "blank" determination was also made. 10-15 mgms of samples 1Q.2 and 1Q.4 were analyzed, and in each case the nitrogen content was estimated as 0.006%. The almost negligible amount of protein in the final polymer is to be expected in view of the acid hydrolytic reaction conditions and the subsequent washing of the polymer.

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# CHAPTER 3

## Experimental Techniques for Rubber Hydrochloride Analyses

### 3.1. Chlorine Analysis by Potentiometric Titration

Samples of partially hydrochlorinated rubber were analyzed for chlorine contents, after oxidative fusion, by a semi-micro potentiometric method. The cell employed was capable of giving an easily recognisable and accurate end-point, was conveniently handled and cleaned, and equilibrium was attained in the system almost immediately after each titrant increment. A graphical method was used to determine the titration end-point. It was estimated that this semi-micro technique permitted the specification of the chlorine content to 0.1% or better, i.e. to 0.5 mole.% hydrochlorination. The accuracy is attested by the smoothness of the plots in figures 1 and 2, and the reproducibility may be demonstrated by the duplicate analyses of sample 1E.8 which gave the values of 32.13 and 32.17% for the chlorine content. Sample 1Q.11 was estimated to contain 32.48% chlorine by the potentiometric titration method and 32.35% chlorine by the Carius method used in a micro-laboratory.

#### 3.1.1. Oxidative Fusion of the Purified Polymer Sample

10-30 mgms of polymer (according to its chlorine content ) were weighed in a platinum crucible on

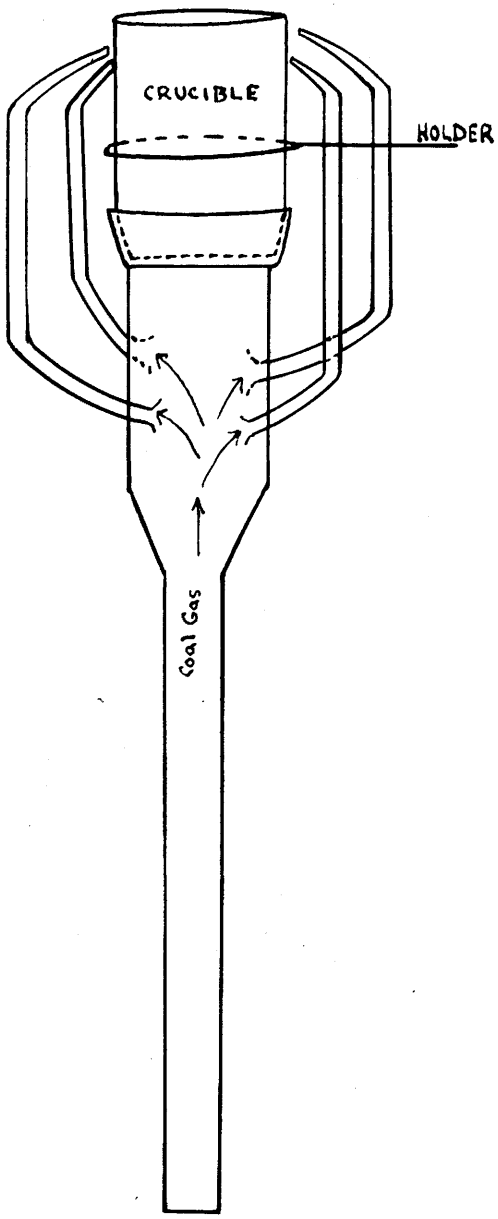
a semi-micro balance and 2 gms of fusion mixture were added. This mixture consisted of a 2:1 ratio of potassium nitrate and sodium carbonate. A special ring-shaped resistance glass burner (fig.3) was designed for melting the fusion mixture evenly from the top of the crucible downwards, so that escaping gases ($CO_2$ and HCl) had to pass through a layer of molten fusion mixture at all times. The crucible lid was kept on throughout the fusion and too rapid heating, which caused frothing, was avoided.

When the fusion had been completed and the crucible cooled, the contents were dissolved in 50-100 mls of freshly distilled water in the titration beaker. Concentrated nitric acid was added dropwise until a pH of approximately 2 was attained. The electrodes and stirrer were immersed in the solution for 15 minutes before beginning the titration.

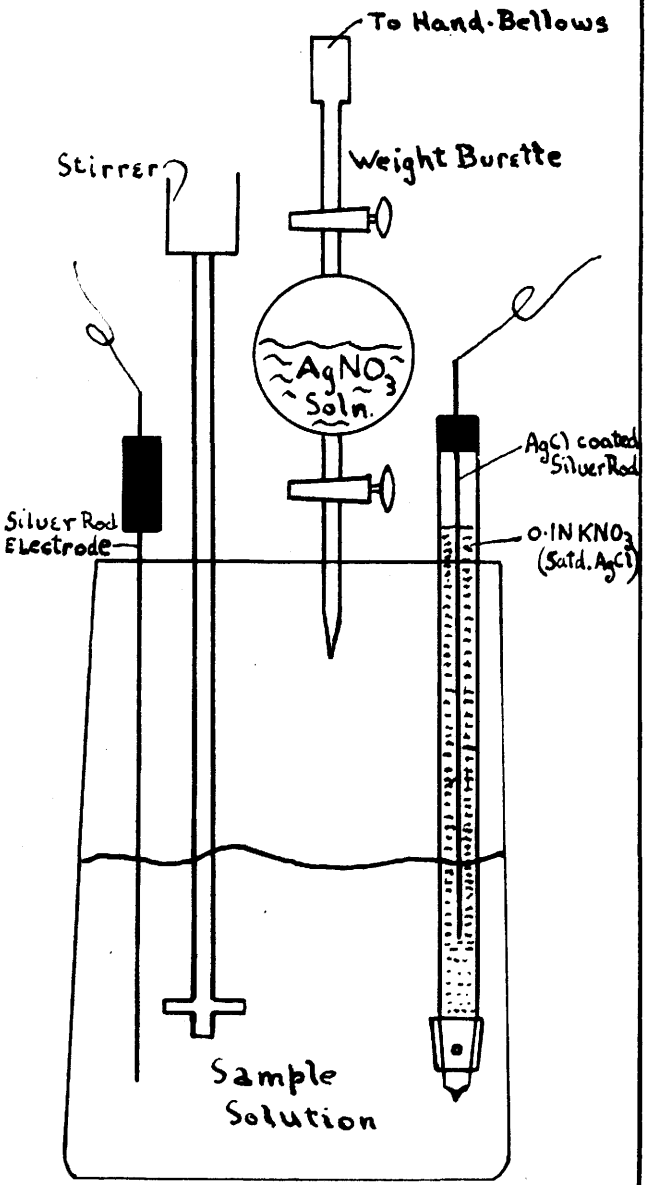
3.1.2. Description of the Potentiometric Cell and Weight Burette

The cell, Ag /Sample Solution // 0.1N $KNO_3$ (Satd. AgCl) /AgCl on Ag

devised by Yeck and Kissin (19) was used in a circuit combining the cell, a potentiometer and a suspension galvanometer. At the equivalence point the $Cl^-$ ion




SPECIAL BURNER FOR FUSIONS. Fig. 3.




TITRATION ASSEMBLY FOR CHLORIDE ANALYSES. Fig. 4.

concentration in the sample solution and at the silver chloride electrode are equal, but the $Ag^+$ ion concentration increases with excess silver nitrate to give an abrupt change in the silver electrode potential.

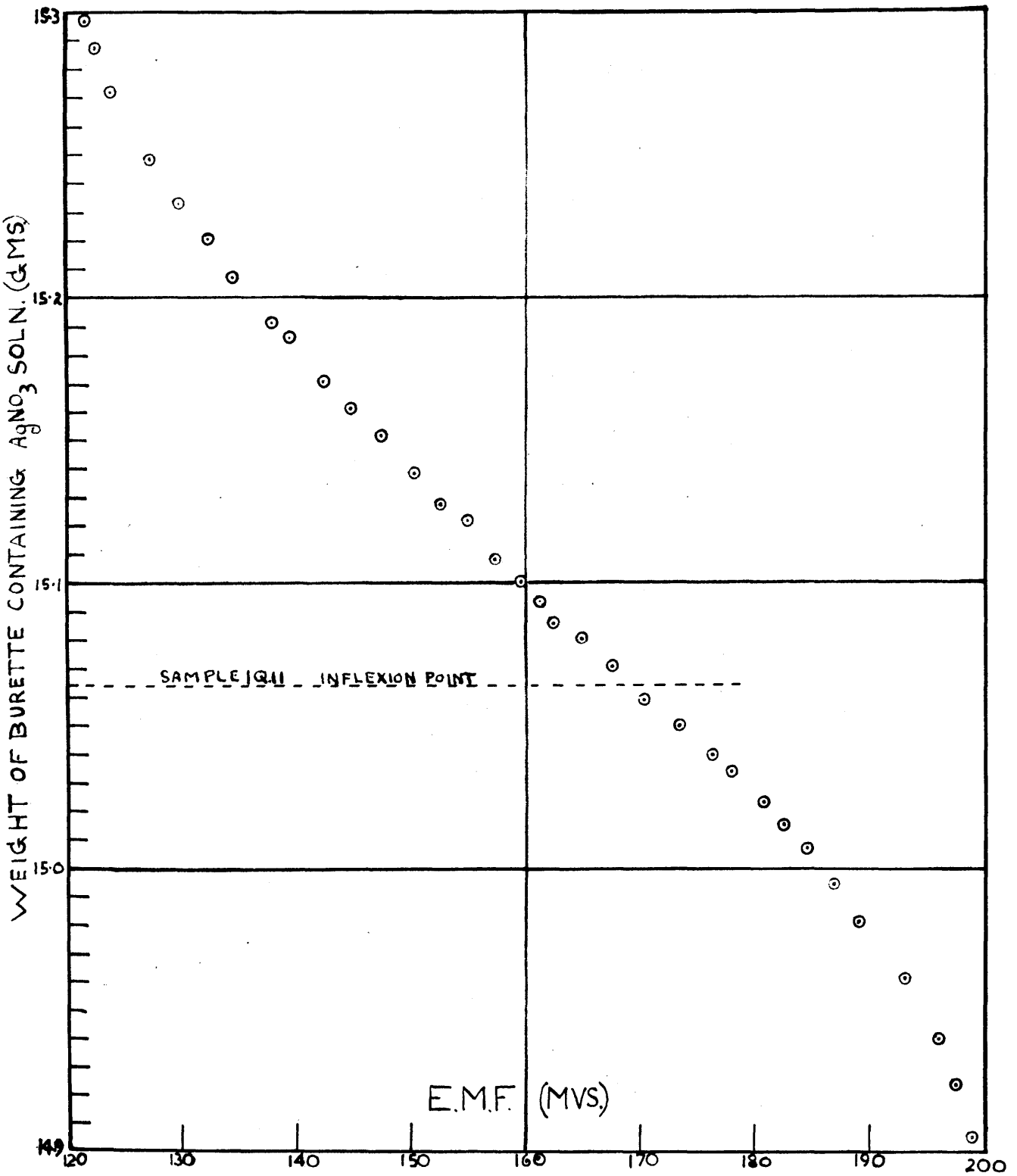
The silver chloride electrode assembly shown in Fig.4 was made from a 7 mm internal diameter, 22 cm long pyrex glass tube, at the bottom of which was a sealed B.7 Quickfit cone. On the side of the cone a very fine hole was pierced. The cone was coated with a warm 6% Agar solution containing 5% ammonium nitrate, and a truncated Quickfit B.7 socket was firmly fitted to it. It was considered that such a coating would reduce leakage and electrical resistance, and 5% ammonium nitrate appeared to be a critical value of electrolyte content in the coating solution. The tube was filled with 0.1N potassium nitrate solution to which was added a small amount of silver chloride to maintain saturation. The silver chloride electrode was sealed into the tube so that it was immersed in the potassium nitrate solution. This electrode was prepared by using a silver rod as the anode during the electrolysis of dilute potassium chloride solution for 2 hours at 2 volts and 0.007 amp. The other electrode for the cell was a silver rod which required careful cleaning immediately before use.

Standardized silver nitrate solution

(approx. 0.05N) was contained in a special weight burette (Fig.4). This was designed with an extremely fine nozzle (coated with wax to prevent wetting by the titrant which would be subsequently lost by evaporation) and with small stopcocks above and below a bulb of 6 ml. capacity. The silver nitrate solution in the bulb was put under pressure by using the hand bellows which could be attached to the upper stopcock. When the bottom stopcock was quickly revolved once, a jet of solution weighing 5-10 mgms was directed into the titration beaker.

3.1.3. Titration Procedure

Previous to starting the titration, the burette was weighed, and the millivoltage which gave no deflection on the galvanometer was read from the potentiometer. Silver nitrate solution was then added to the sample solution until the approach of the end-point was detected. The end-point region was taken to start when the addition of 10 mgms of the titrant caused an increment (dE) of 0.5 mvs in the voltage of the system, and was taken to end when similar conditions prevailed after passing the end-point (i.e. the maximum dE, usually about 5 mvs for 10 mgms titrant). In the end-point region the burette was reweighed, and the voltage of the system was read, after each titrant addition (5-10 mgms). The amount of silver nitrate solution added during the end-point region/




A POTENTIOMETRIC TITRATION CURVE FIG. 5

E.M.F. OF SYSTEM AGAINST WEIGHT OF TITRANT ADDED IN REGION OF END-POINT.

was usually about 10% of the total titration, and a sigmoid graph of E.M.F. against weight of titrant added was plotted for this range (Fig.5). The inflexion point of such a graph(i.e. the end-point) could be read to within 5 mgms silver nitrate solution by several observers, provided they used a thin glass fibre to outline the best smoothed curve through the experimental points. From the weight of polymer used, and silver nitrate solution required, C, M, and W were evaluated as shown below.

3.1.4. Standardization of Silver Nitrate Solution and Allowance for $Cl^-$ in Fusion Mixture: Sample Calculations

The amount of $Cl^-$ ion in the fusion mixture was determined by standardizing the silver nitrate solution first against potassium chloride which had been previously recrystallized, and then against the recrystallized potassium chloride + 2 gms fusion mixture.

a) Standardized without fusion mixture

Weight of KCl used = 10.36 mgms
Weight of $AgNO_3$ solution required = 2.91459 gms

$$KCl + AgNO_3 = KNO_3 + AgCl$$

74.553 169.888

$\therefore$ 10.36 mgms KCl $\equiv \frac{10.36 \times 169888}{74553}$ mgms $AgNO_3$

$\equiv$ 0.02361 gms $AgNO_3$

$\therefore$ 2.91459 gms titrant contain 0.02361 gms $AgNO_3$

$\therefore$ 1000 " " " 8.100 gms $AgNO_3$

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b) Standardization with 2 gms Fusion Mixture (F.M)

9.89 mgms KCl + 2 gms F.M. required 2.78805 gm titrant

In a) it was found that
2.91459 gms titrant were reqd.for 10.36 mgms KCl without F.M.

$\therefore$ on this basis
2.78805 gms titrant should be reqd.for 9.91 mgms KCl

$\therefore$ the equivalent of 0.02 mgms KCl (9.91-9.89) is found in 2 gms F.M.

Similarly

10.64 mgms KCl + 2 gms F.M. reqd. 2.99665 gms titrant

and from a) 2.99665 gms titrant $\equiv$ 10.66 mgms KCl without F.M.

$\therefore$ again 0.02 mgms KCl (10.66-10.64) is found in 2 gms F.M.

In calculating % $Cl^-$ in the polymer, the silver nitrate solution was taken to contain 8.1 gms $AgNO_3$/1000 gms titrant, i.e. no account was taken of F.M., and therefore in each analysis, 0.0095 mgms $Cl^-$ was subtracted from the amount found by titration.

(Note: the silver nitrate solution was standardized by the Mohr titration method and gave results in excellent agreement with the above standardization).

c) Sample Calculation from Titration Result (Sample 1Q.11)

Initial Weight of burette = 19.148 gms
Final weight of burette at end-point (See Fig.5) = 15.065 gms

∴ Weight of $AgNO_3$ solution reqd. = 4.083 gms
Weight of polymer used = 21.20 mgms

1000 gms titrant contain 8.1 gms $AgNO_3$

∴ 4.083 " " " 33.08 mgms $AgNO_3$

$Ag^+/AgNO_3 = 0.635$

∴ $Ag^+$ reqd. = 33.08 x 0.635 = 21.01 mgms

$Cl^-/Ag^+ = 0.328$

∴ $Cl^-$ content = 21.01 x.328 = 6.891 mgms

Actual $Cl^-$ content = 6.891-0.0095 = 6.8815

$$\therefore \text{Wt.\% Cl in polymer} = \frac{6.8815 \times 100}{21.20} = 32.48$$

$$\therefore \text{Wt.\% Hydrochlorination} = 32.48 \times \frac{104.58}{35.457} = 95.80$$

$$\text{and Mole.\% Hydrochlorination} = \frac{32.48 \times 186.8}{97.2 - 32.48} = 93.70$$

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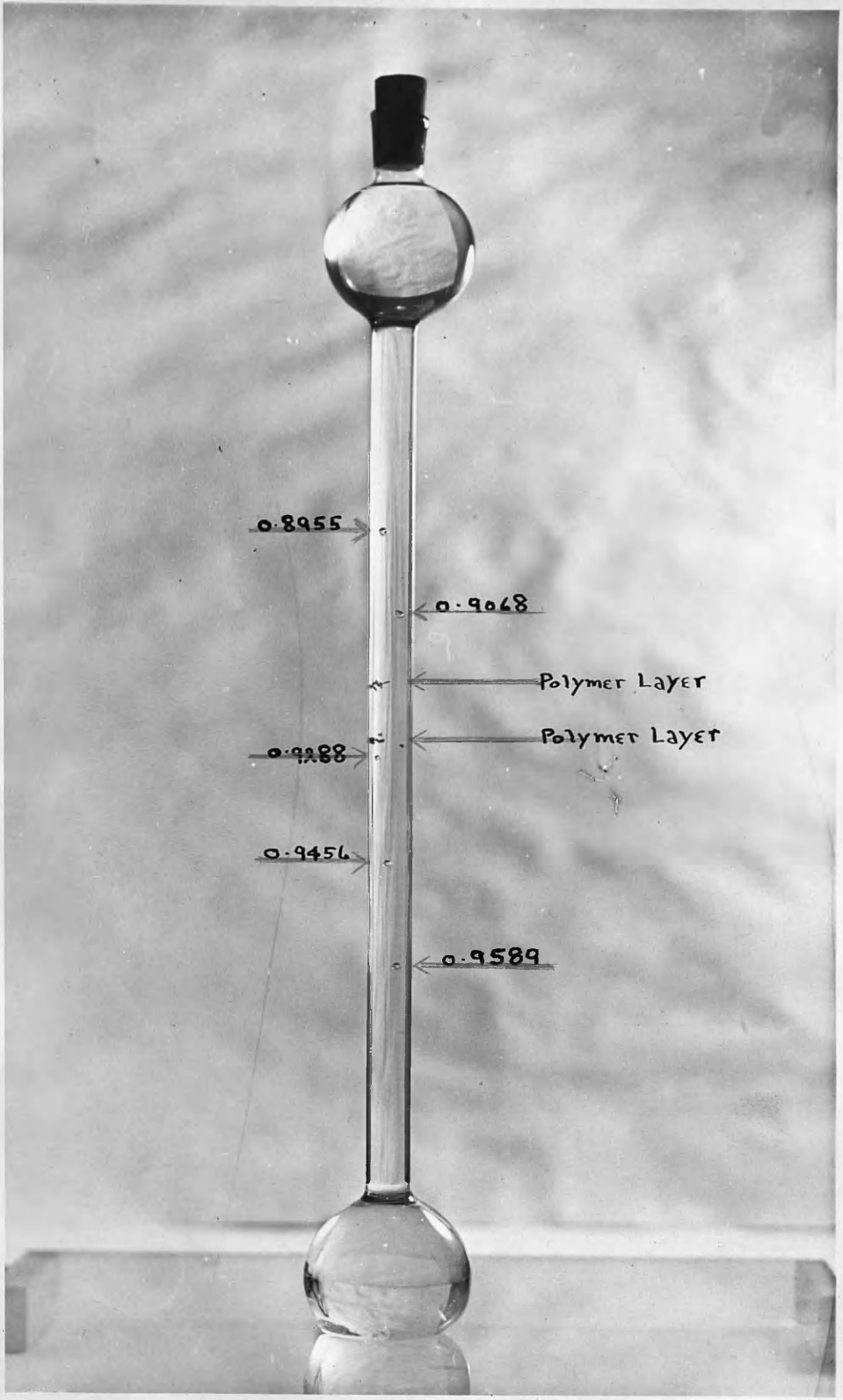
## 3.2. Density Measurements on Polymer Samples

The use of a density-gradient tube to make measurements on polymers was first applied by Boyer, Spencer, and Wiley (20). The method was improved by Gordon (12) who adapted simplified Berg (21) immersion hydrometers or "glass floats" as reference standards which could be used to calibrate density as a function of height in the tube. The density gradient in the tube is established by the vertical inter-diffusion of two miscible liquids (which have no physical or chemical effect on the polymer). Particles of polymer film dropped into the tube sink to the level at which their density equals that of the surrounding liquid.

### 3.2.1. Manufacture and Calibration of Glass Floats

Full details of the manufacture and calibration of the glass floats have been given by Gordon and McNab (22). The floats were made of almost spherical shape and about 2-3 mm diameter from thin-walled capillary drawn originally from 1.5 cm diameter pyrex tube. Some practice in controlling the glass-to-air ratio was required to obtain floats of the desired approximate density. The spheres were stored for a week after manufacture before their densities were determined, because imcomplete annealing caused an initial small increase in density.




Photograph of Density-Gradient Tube 1. showing Positions of Floats and Polymer Layers at Room Temperature.

F.I.G. 6

The density of the glass floats was found essentially by the method of Berg (21) involving flotation of the glass sphere in a density bottle containing a solution of the required density. The float density was found to 0.0001 gm/cc. Five floats were recalibrated after two years constant use, and the increases in density of each at the end of that period were 0.00004, 0.00012, 0.00017, 0.00024, and 0.00027 gm/cc respectively. These figures were mostly just outside experimental error but were negligible for the polymer density measurements made. The density of partially hydrochlorinated rubber lies between 0.9040 and 1.1550 at 26.7°C, and 19 glass floats were calibrated to cover this range.

3.2.2. Preparation and Use of Density-Gradient Tubes

Dumb-bell shaped vessels (Fig.6) were used to contain the density gradient. The gradient was prepared by filling the tube to the half-way mark with the heavier solution, and then slowly adding the lighter solution dropwise down the side of the vessel so as to preserve the interphase. The floats were then introduced, and rested on the interphase. A fine glass stirrer was then moved slowly up and down through the interphase with strokes of increasing amplitude. Inter-diffusion of the solutions then caused the formation of the density gradient which was observed in terms of the vertical spread of the floats.

It was essential to previously de-gas the solutions in order to prevent the formation of air bubbles on the floats and polymer particles.

The height of the floats in the tube was measured using a cathetometer. The plot of density against height is sigmoid, approaching the vertical at each end, i.e. at the height of the dumb-bell resevoirs where the density is constant with height. The central portion of the plot is linear (Figs. 7-10) and remains so for long periods although the spread of the floats may increase.

10 mgms, or less, of the dry purified polymer sample were placed between two clean glass slides and pressed in a spring-loaded clip for three minutes in a 100°C steam bath. The resulting film was cut cleanly into 1 $mm^2$ portions, about six of which were transferred to the appropriate density-gradient tube. The tube was immersed in a 26.7°C water thermostat for two hours. The heights of the floats and the particles were then observed through the thermostat window. The height of the plane of polymer particles was obtained by averaging the individual particle heights, and the density of the sample was evaluated graphically (Figs 7-10). The density was then expressed as specific volume and, from Fig.1, the mole.% hydrochlorination was interpolated.

The polymer particles could be withdrawn from the tube by "fishing" them out on the silicone grease-coated tip of a glass fibre. Care was taken, of course, to prevent touching the floats, and the slow motions of a thin glass fibre did not upset the density gradient to any marked degree.

Table 2 below gives the solutions used in each of the four density-gradient tubes which were used to cover the required density range, and the densities of the floats contained in each tube. The sodium thiosulphate - potassium iodide solutions, apart from giving the required density, helped to minimize the danger of the polymer particles being oxidized. For this reason also, a little pyrogallol was sometimes added to tubes 1 and 2, but this refinement was found to be unnecessary (especially with natural rubber hydrochlorides) provided no undue delay was incurred in recording the density of the sample particles after they had reached their equilibrium level at 26.7°C.

Polymer densities measured by this method were accurate to 0.0010 gm/cc or (usually) better, i.e. to 0.3% reaction. Fig. 6 illustrates the accuracy by showing density-gradient 1. containing two layers of particles from two polymer samples of different per cent hydrochlorination. Fig.7 is the relevant height

against density plot. The data at 26.7°C for each layer are recorded below:

| | Upper Layer | Lower Layer |
|---|---|---|
| Height | 26.76 cms | 25.00 cms |
| Density | $0.9156 \pm .0002$ | $0.9240 \pm .0008$ |
| Mole.% Hydro-chlorination | 4.00% | 7.25% |

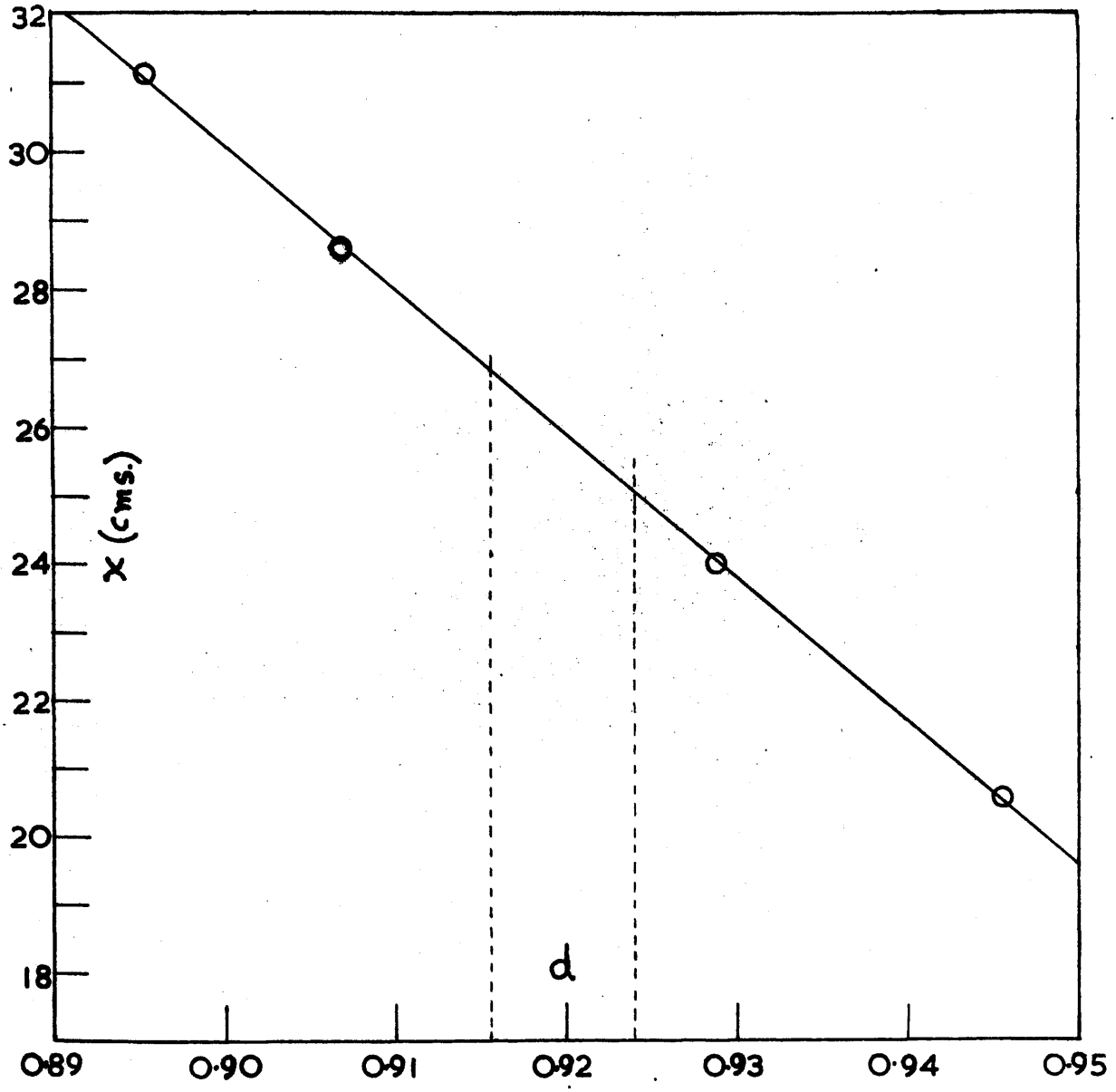
Fig.6 is photograph of the Tube at Room Temperature

TABLE 2

Solutions and Floats for Density-Gradient Tubes

| Tube | Bottom Solution (Parts by Volume) | Top Solution (Parts by Volume) | Floats (Density) |
|---|---|---|---|
| 1 | 12pts.ethanol : 88pts.water | 75pts.ethanol : 25pts.water | 0.8955<br>0.9068<br>0.9288<br>0.9456<br>0.9589 |
| 2. | 22pts.lactic acid : 78pts.water | 40pts.ethanol : 60pts.water | 0.9719<br>0.9791<br>0.9882<br>1.0006<br>1.0232 |
| 3. | 20pts.saturated $KI-Na_2S_2O_3$ soln. : 80pts.water | Water | 1.0416<br>1.0663<br>1.0853<br>1.1092 |
| 4. | 30pts.saturated $KI-Na_2S_2O_3$ soln. : 70pts.water | 15pts.saturated $KI-Na_2S_2O_3$ soln. : 85pts.water | 1.1167<br>1.1359<br>1.1529<br>1.1670 |

----------oOo----------



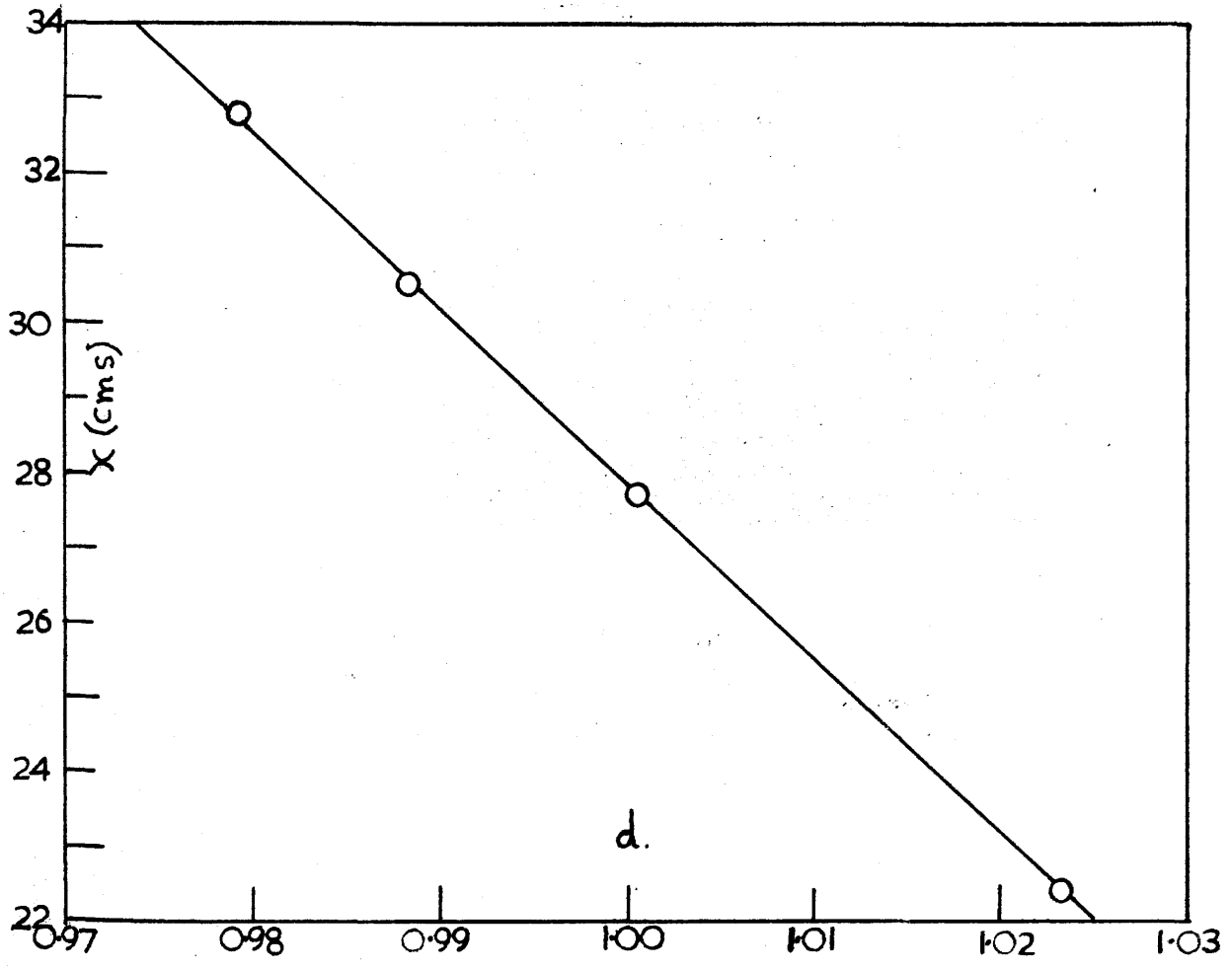

PLOT OF HEIGHT, (x cms) AGAINST DENSITY, (d) FOR CENTRAL PORTION OF TUBE 1 (Fig. 6)

FIG. 7

O ..... PYREX FLOATS

DENSITY OF UPPER LAYER AT 26·7°C IS 0·9156 ± ·0002

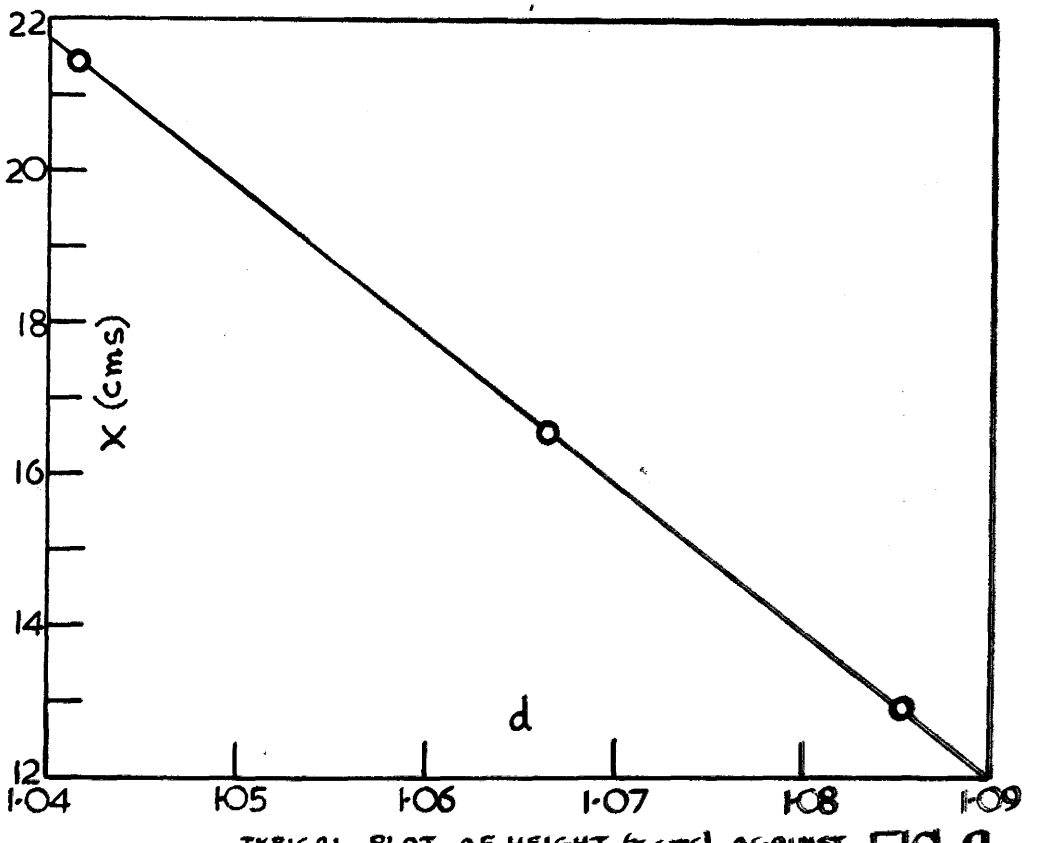
DENSITY OF LOWER LAYER AT 26·7°C IS 0·9240 ± ·0008




TYPICAL PLOT OF HEIGHT, (x cms) AGAINST DENSITY, (d) FOR CENTRAL PORTION OF TUBE 2
O···· REPRESENTS PYREX FLOATS.

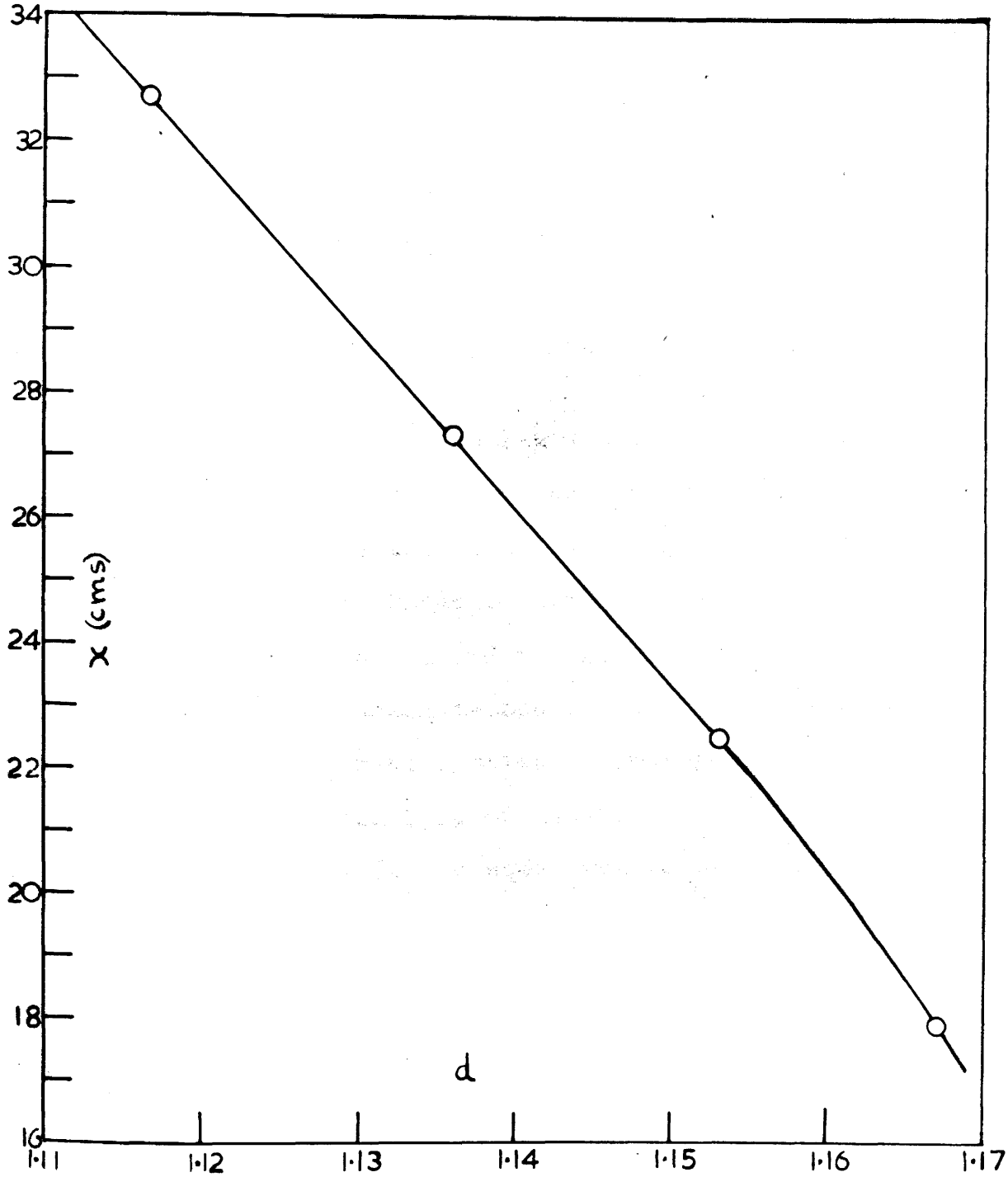
FIG. 8

PLOT IS EXPANDED FOR ACCURATE DETERMINATION OF d.




TYPICAL PLOT OF HEIGHT, (x cms) AGAINST DENSITY, (d) FOR CENTRAL PORTION OF TUBE 3. FIG. 9
O.... REPRESENTS PYREX FLOATS.

PLOT IS EXPANDED FOR ACCURATE DETERMINATION OF d.




TYPICAL PLOT OF HEIGHT, (x cms) AGAINST DENSITY, (d) FOR CENTRAL PORTION OF TUBE 4.
O···REPRESENTS PYREX FLOATS.
PLOT IS EXPANDED FOR ACCURATE DETERMINATION OF d.

FIG. 10.

# CHAPTER 4

## Experimental Techniques and Apparatus for Latex Hydrochlorination

### 4.1. Preparation of Acid Latex

Quantities of latex from the same original drum of Dunlop 60% Hevea latex (centrifuged) were acidified as required throughout the duration of the experimental work.

Nitrogen gas was bubbled through the quantity of latex to remove the ammonia present, and the solids content of the latex was then determined by the usual evaporation method. 1.5% Vulcastab L.W. (on the solids content) was added in the form of a 20% aqueous solution to the ammonia-free latex. (Vulcastab L.W., marketed by Imperial Chemical Industries, is an ethylene oxide condensation type of non-ionic stabilizer, $R-(CH_2-CH_2O)_n-H$. ). An equal volume of concentrated hydrochloric acid was then quickly poured into the volume of latex under vigorous stirring, and after filtering through fine-mesh glass cloth, the latex was stored in a flask. It could then be reacted with hydrogen chloride gas without coagulation.

### 4.2. Flocculation and Purification of Polymer Samples

The occurence of coagulation when latex is added to an excess amount of water, is usually ascribed

to an equilibrium displacement of the stabilizing colloids. For effective flocculation and efficient purification, the formation of small polymer particles (.1 to 1 mm ), whose aggregation is reversible, is required. Little acid from the latex serum is then occluded in the polymer.

It was found possible to obtain these conditions when the sample (approx.0.5 cc ) of partially hydrochlorinated Hevea latex (solids content about 30%) was sprayed gently, in a fine jet, into about 200 times its volume of boiling water which was slowly swirled in a beaker. The suction tubes used to withdraw latex samples from the reaction vessel were therefore constructed with finely constricted nozzles.

Heavily hydrochlorinated rubbers were powdery and could be easily washed, but stricter washing precautions were required for pure rubber and lightly reacted rubber samples which were still in the rubbery state. These small particles were allowed to settle in the flocculation beaker, and were then slowly and carefully poured into a No.3 sintered glass filter where suction was carefully applied, and the polymer particles allowed to form a thin mat on the smooth sintered glass base of the filter. Washing was carried out using freshly distilled water which was drawn through the matted

structure of the polymer. The thin polymer film was then cleanly peeled off the filter base and thoroughly dried in storage under high vacuum (mercury diffusion pump, .02 mm Hg) until it was prepared for density and chlorine content determinations.

## 4.3. The Initial Density of Unhydrochlorinated Hevea Rubber

It was necessary to determine accurately the initial density of pure Hevea rubber ($d_o$) at 26.7°C, because a reliable value of $1/d_o$ (M and W=0) was required for the specific volume against per cent hydrochlorination plots (Figs.1 and 2 ). Also, a knowledge of the constancy of $d_o$ as the latex aged under alkaline or acid conditions was required.

The rubber density at 26.7°C was measured immediately after each amount of latex had been acidified, and in some cases, was redetermined after storage in the acid condition (approx.25% HCl in the serum). $d_o$ was evaluated as 0.9040 and the constancy of this figure is illustrated in Table 3.

The density of rubber has been previously reported in the literature as 0.9065 at 20°C (23) (24), and 0.9000 and 0.9060 at 25°C (12) (25). The value of 0.9040 measured here is accepted with some confidence considering the purification undergone by the latex when it is

acidified, flocculated, washed, and measured with precautions against oxidation.

TABLE 3

Constancy of the Initial Density of Hevea Rubber

| Age of Hevea 60% Latex stored in Ammoniacal conditions (days) | Density of Rubber ($d_o$) at 26.7°C immediately after acidification | Density of Rubber ($d_o$) after storage in acid conditions |
|---|---|---|
| 0 | 0.9048±.0010 | - |
| 60 | 0.9040 .0005 | - |
| 90 | 0.9038 .0005 | (?) 0.9085 (90 days) |
| 180 | (?) 0.9063 .0005 | 0.9040 (20 days) |
| 210 | 0.9039 .0005 | 0.9040 (30 days) |
| 270 | 0.9037 .0002 | - |
| 330 | 0.9038 .0005 | 0.9042 (90 days) |
| 450 | 0.9042 .0010 | - |
| 510 | 0.9040 .0005 | 0.9040 (90 days) |
| 600 | 0.9036 .0010 | - |

Ave. $d_o$ = 0.9040

------ooOoo------

## 4.4. Apparatus employed for Latex Hydrochlorination

### 4.4.1. Thermostats

Experiments and density measuremen ts at 26.7 °C were carried out in a water-thermostat tank provided with observation windows. The temperature was controlled by an adaption of the thermostatic relay working from A.C. mains devised by D.Taylor (26). The circuit combined a mercury contact regulator and a 25W

pre-heater in parallel with two 250 W heating lamps. The temperature was controlled to 0.01°C, provided the water in the tank was adequately stirred.

A Dewar flask containing White Technical Oil was used as an oil bath in which to carry out reactions at 69.5°C. The same type of thermostatic relay and mercury contact regulator were used. A transformer was incorporated in the circuit to pass 2.6 amps at 20 volts through a 5.6 ft. coil of nichrome wire which was used for a heating element. The oil was stirred and its temperature controlled to 0.1°C.

For latex hydrochlorination at 0°C, the reaction vessel was immersed in iced water in the Dewar flask. Crushed ice was then packed into the flask around the apparatus. The ice and water were stirred at the bottom of the flask and the temperature could be maintained at 0°C±0.1°C for long periods.

4.4.2. Starting Time of Reaction

Latex hydrochlorination was carried out under controlled conditions of hydrogen chloride pressure and hydrogen chloride equilibrium concentration in the serum. Inorder to attain these conditions, the latex serum was saturated with HCl at the relevant pressure and temperature of the experiment. At a given temperature, the rate of latex hydrochlorination increases rapidly

with HCl pressure (see Chapt.5), although the HCl concentration in the serum may only increase by a few per cent. At 1 Atm. HCl, the rate of latex hydrochlorination is relatively slow, and at lower HCl pressures the reaction rate will be small but, nevertheless, measurable. Therefore during the time taken to saturate the latex at, say, 1 Atm. (i.e. while the HCl pressure is building up to 1Atm.), there will be some reaction taking place at a slow rate. It is convenient to take as the starting time of the reaction, the moment when the serum is saturated at the required temperature and pressure, because this can be observed easily. The saturation period must then be made as short as possible in order to reduce to negligible amount the slow hydrochlorination during this period. The bulk hydrochlorination rate (i.e. occuring within the bulk of the latex particle) is indeed slow at pressures less than 1 Atm. But there is superimposed on this, at the beginning of the reaction, a particle surface hydrochlorination. This latter reaction affects only about 3% of isoprene units in natural rubber latex, but can affect up to about 20% of the units in synthetic polyisoprene latex. Moreover, this particle surface reaction can occur at measurable rates at HCl pressures as low as 0.08 Atm. Therefore, especially with synthetic latices, if the reaction at 1 or 2 Atm

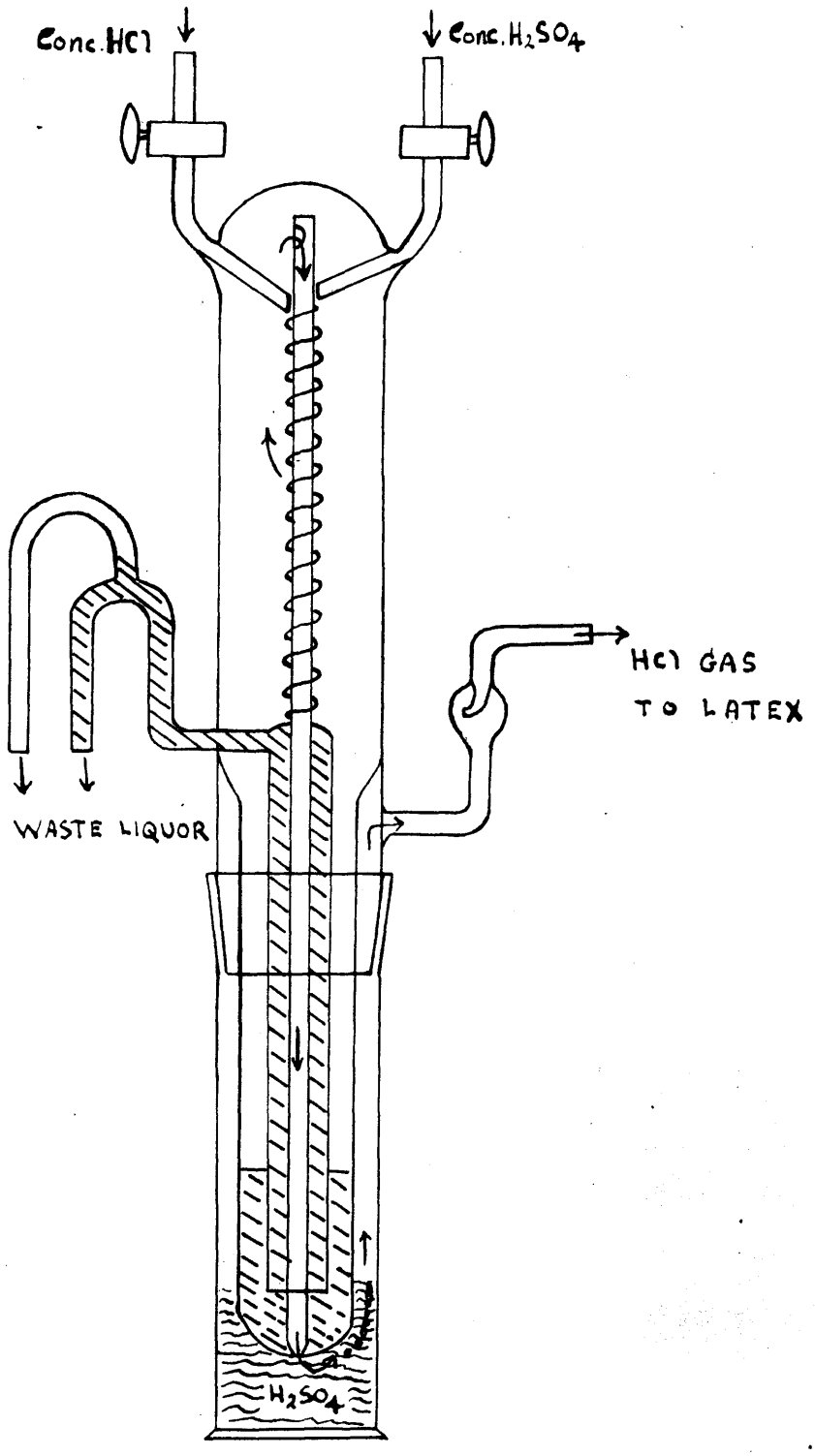
is taken to start when the serum is saturated at these pressures, saturation must be rapidly attained. The micro-generator and technique described in section 4.4.4. was therefore most useful in this respect.

The acidified Hevea latices were stored (at room temperature, about 15°C) with an HCl concentration in the serum of 25%, i.e. equivalent to an HCl pressure of 1 mm (interpolated from International Critical Tables). No hydrochlorination of the rubber particles was expected at this extremely low pressure, and the constancy of the polymer density during storage reflected the absence of any reaction.

4.4.3. Apparatus for Latex Hydrochlorination at Atmospheric Pressure

The type of hydrogen chloride gas generator devised by Libman (27) was constructedin pyrex glass (Fig.11). The gas flow was continuous and could be regulated. Concentrated sulphuric and hydrochloric acids were siphoned from Winchesters fitted with a Mariotte bottle, and allowed to drop on to the helix round the central tube. The hydrogen chloride evolved passed down through the hole in the central tube as shown. The pressure in the gas space caused the waste liquors running off the helix to be expelled.

After leaving the generator, the gas was




CONTINUOUS HCl GAS GENERATOR (DUE TO LIBMAN).

FIG. 11

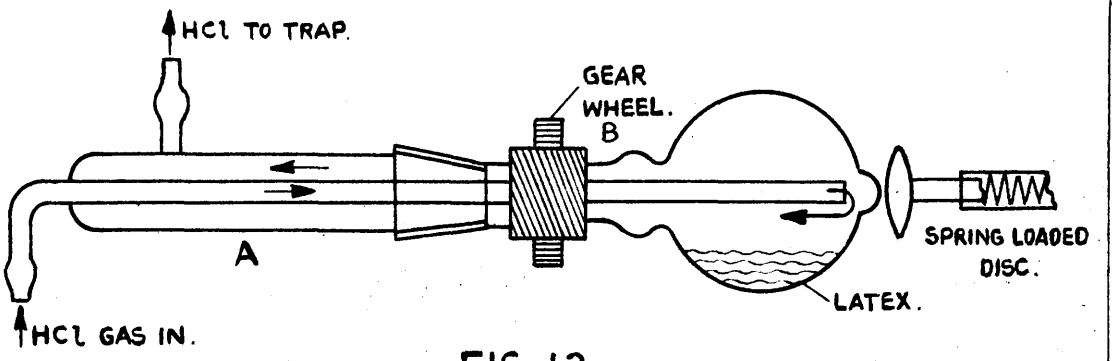



FIG. 12

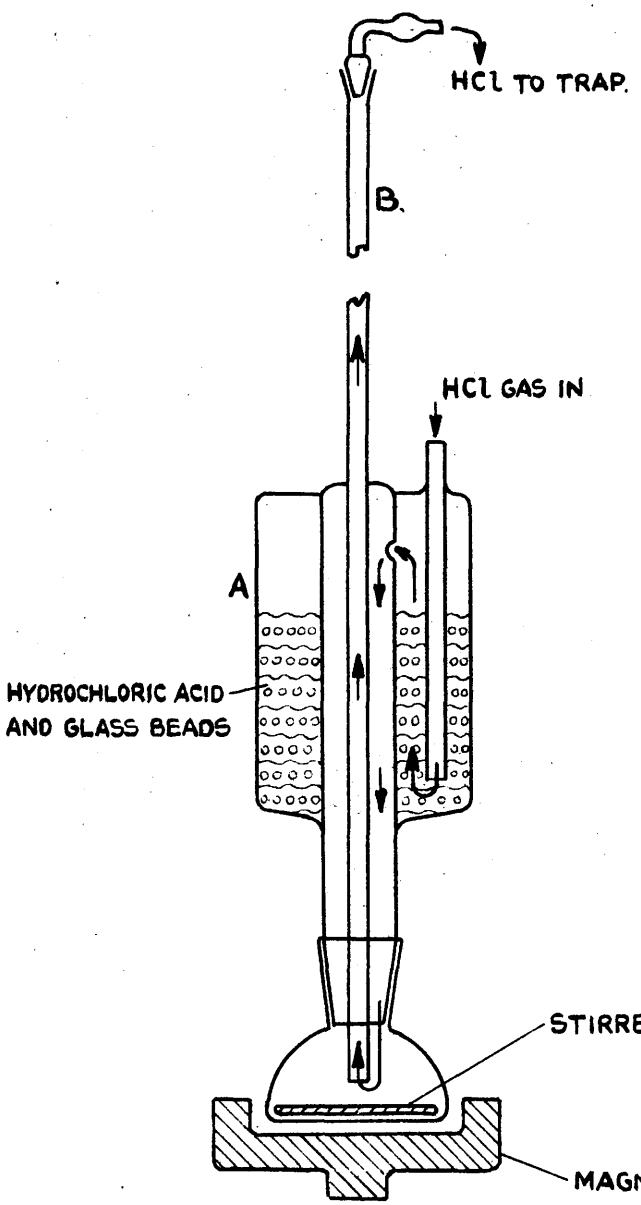



FIG. 14

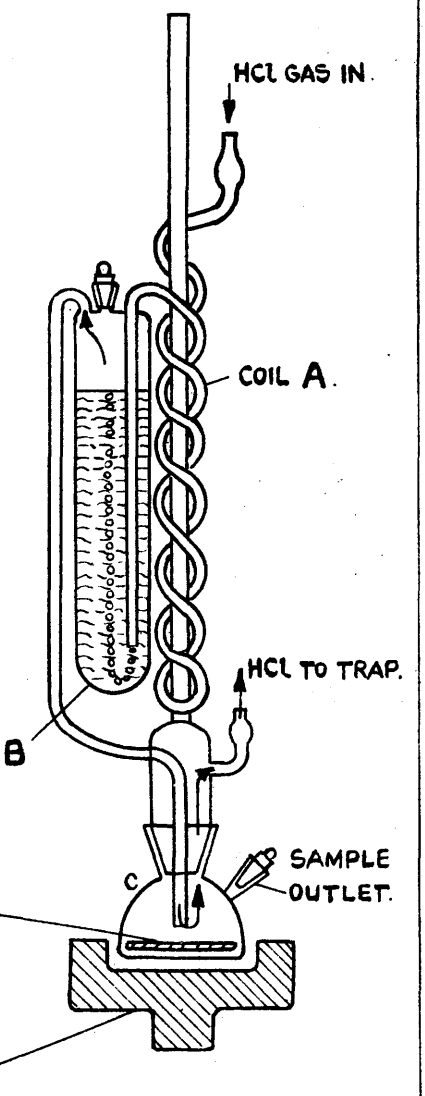



FIG. 13

heated,or cooled, in a coil to the reaction temperature, and then bubbled through an aqueous hydrochloric acid solution which had been previously saturated at atmospheric pressure at this temperature. The latex in the reaction vessel was continually stirred, and to avoid frothing difficulties, the hydrogen chloride gas was simply passed over the latex, not through it. Finally, the excess gas flow was lead to an absorption trap at atmospheric pressure.

Figs. 12, 13, and 14 show types of reaction vessels in which the latex was hydrochlorinated at Atmospheric pressure.

The reactor shown in Fig.12 was the first type employed. In it, the latex was not directly stirred, but fresh surfaces were continually exposed to the gas as the reaction chamber rotated on its horizontal axis. The inlet-outlet tube A was clamped to a framework on the thermostat, and the gear wheel B , fitted to the rotating chamber, meshed with one on the framework which was driven by a spring-band from an electric motor. The framework could be swung down so that the reactor was immersed in the water of the thermostat. The cone and socket were carefully lubricated with the minimum amount of paraffin oil, and spring loading prevented lateral slipping. This reactor could not be left unattended for long periods, could not be used at high or low temperatures, and was

inconvenient for sampling.

The second reactor (Fig.13) incorporated the heating coil A and gas saturator B. The gas flow is indicated by arrows. The latex in the reaction flask C was stirred magnetically. The stirrer was a small iron rod sheathed in pyrex glass. The apparatus still suffered from the fault that it had to be lifted out of the thermostat for latex samples to be withdrawn.

The concentric design of the reactor shown in Fig.14 surmounted this difficulty. The hydrogen chloride gas was heated (or cooled) in the chamber A as it bubbled up through the glass beads and previously saturated hydrochloric acid solution. Samples were withdrawn by inserting thin glass suction tubes down the gas outlet tube B.

The reaction flasks were designed to hold about 4 cc of latex, and therefore a number of samples could be withdrawn throughout one run. When the latex serum was saturated at atmospheric pressure, fumes due to hydrogen chloride vapour quite suddenly emerged from the reaction flask. This was taken to signalize the start of the reaction and could be noted to within a minute. With a fast gas flow, the time taken to saturate 4 cc latex (i.e. before HCl fumes observed) was three minutes or less. To check that the appearance of HCl

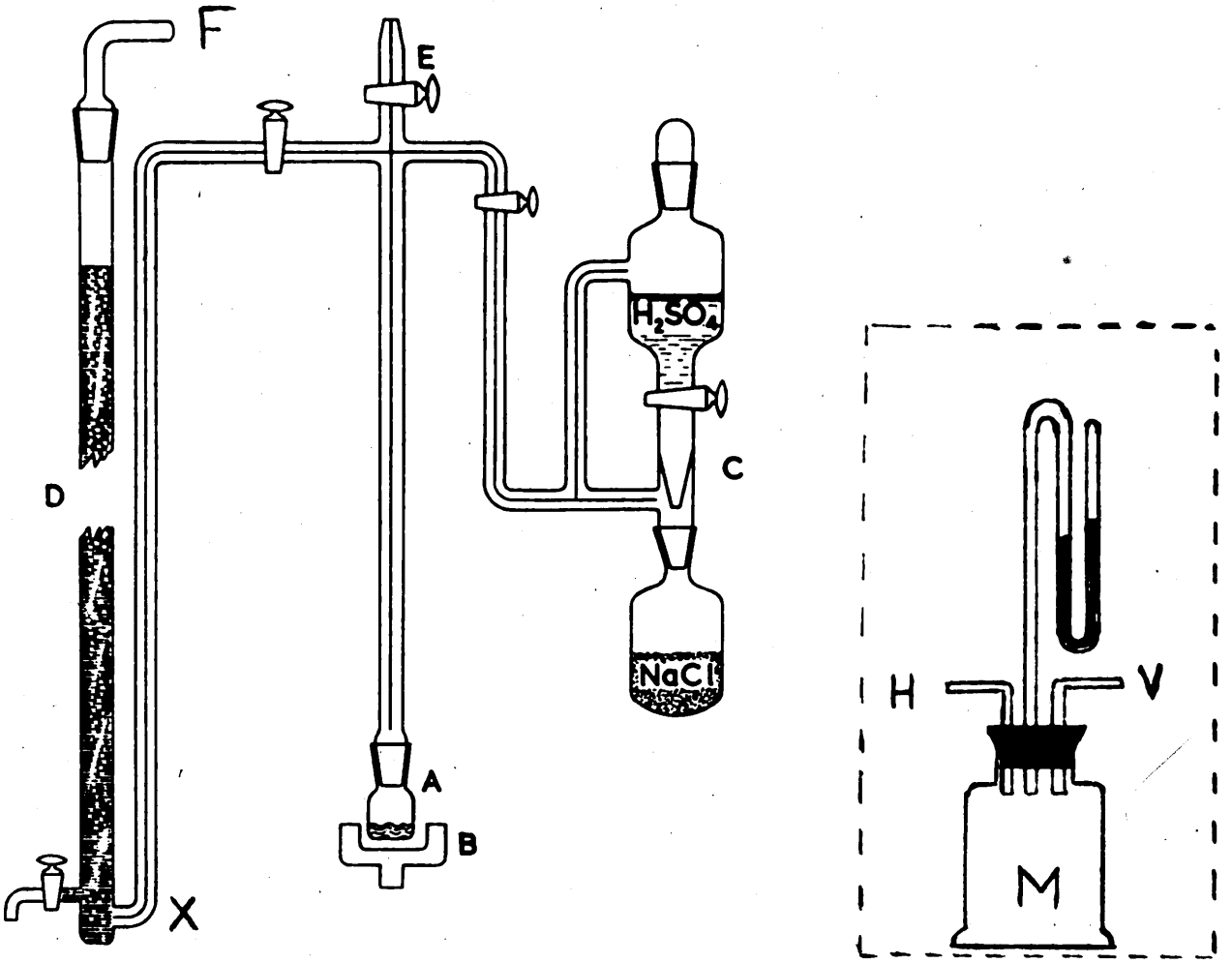



FIG. 15

Micro-reactor for Latex Hydrochlorination.

fumes reliably indicated serum saturation, 4 cc of equivalent acid solutions were saturated at the same temperature and pressure under the same stirring and gas-flow rates. The time was noted for the density of the acid solution to reach its maximum (measured by allowing acid drops to fall in a carbon tetrachloride-paraffin oil density-gradient tube). Polythene tubing was used to lead the gas to and from the reactors.

4.4.4. Micro-Reactor for Latex Hydrochlorination at Higher Pressures.

The micro-reactor illustrated in Fig.15 was primarily designed for hydrochlorinating latex at 2 Atm. pressure, but it could be used for reactions at atmospheric pressure also. It permitted high speed of starting and stopping the reaction (the time to saturate the latex at 2 Atm. was about 10 seconds).

The small flask A (capacity 2.5 cc ) contained about 200 mgms of latex and a small stirrer revolved by the magnet B. The hydrogen chloride gas generator C contained sulphuric acid and sodium chloride, and the mercury lute D acted as a manometer. The flask A was immersed in an ethanol-solid $CO_2$ mixture to freeze the latex. Mercury was added to the lute D to a height of about 3 inches. The whole system was then evacuated through the stopcock E causing the mercury to rise up in the capillary limb of D. With the stopcock E closed, the

system was filled with HCl gas to atmospheric pressure (mercury level the same in each limb of the manometer). The system was again evacuated, and the pressure of hydrogen chloride gas again built up to atmospheric. Sufficient mercury was then added to the wide limb of the lute, so that when sufficient gas was generated to force all the mercury out of the capillary limb into the wide limb, the total pressure of the system would be 2 Atm. (Mercury height in wide limb above X plus atmospheric pressure). When the pressure reached 2 Atm, the reaction vessel was transferred to the thermostat and the latex was melted and stirred. As the serum absorbed hydrogen chloride gas and became saturated, the pressure in the system fell , and mercury rose up in the capillary limb of the lute. However, if care was taken to generate sufficient HCl gas to compensate for this, the serum could be saturated at 2 Atm. in 5-10 seconds, and the starting time was taken as the moment when the gas once more bubbled up through the mercury in the wide limb of D and escaped at F to the trap. Excess gas generation was maintained throughout the reaction duration. The reaction was effectively stopped by releasing the pressure on opening the stopcock E to slight vacuum. The flask A was promptly opened and the latex transferred to boiling water. All the stopcocks and Quickfit joints were spring loaded, and the connections

between gas generator, reaction vessel, and lute were made with Polythene tubing for ease of manipulation (although the whole apparatus is shown united in Fig.15)

4.4.5. Adaption of Micro-Reactor for Hydrochlorination under Reduced Pressure

Experiments on synthetic polyisoprene latex carried out under reduced pressure are described in Chapter 10. The micro-reactor described above was adapted for reactions at reduced pressure by incorporating the manometer M shown in inset of Fig.15.

The manometer M was connected at H to the mercury lute at F. The correct amount of mercury to give the desired hydrogen chloride gas pressure in the system (allowing for vacuum attained by water pump, and the height of mercury originally in the capillary limb) was added to the lute. When the latex had been frozen, the system was evacuated three times as described above. After the third evacuation, instead of rebuilding the pressure to atmospheric, the stopcock E was closed, and the vacuum line was attached at V to manometer M. HCl was generated and bubbled up through the mercury in the wide limb of the lute, and was carried off by the vacuum on the other side. The gas pressure in the reaction flask A was then given by the height of mercury in the lute above X plus the difference in levels of the mercury in M.

The reaction was stopped by withdrawing the vacuum at V, simultaneously opening the stopcock E, and quickly removing the flask A to flocculate the reacted latex.

4.5. Effect of Water Vapour Pressure

At 69.5°C, 1 and 2 Atm. pressure, and at reduced pressures, the equilibrium water vapour pressure became appreciable. The effect was calculated by interpolation from the International Critical Tables, and subsequent data recorded in this thesis refer to the actual HCl pressures. Thus, for latex hydrochlorinated at 69.5°C at a total pressure of 2 Atm, the HCl pressure was 1.95 Atm.

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# CHAPTER 5

## Kinetics of Hevea Latex Hydrochlorination

### 5.1. Reproducibility of Data

The kinetics of Hevea latex hydrochlorination were studied under conditions of 1 and 2 Atm. pressure and at 0, 26.7, and 69.5°C.

The progress of the reaction was followed by density measurements on the purified polymers. These measurements were interpolated to Mole.% hydrochlorination (Fig.1). The kinetic curves of Mole.% hydrochlorination against Time for the relevant experimental conditions are illustrated in Figs. 16-21.

When the latex hydrochlorination was first carried out at atmospheric pressure, a great number of points were required for the rate curves in order to determine, without ambiguity, their exact shape. When the features of the rate curves were reliably ascertained, and as the experimental technique improved, fewer samples were required to permit a kinetic analysis of the reaction.

There is reason to be satisfied with the reproducibility and smoothness of the kinetic curves (Figs. 16-21). Each curve was plotted from combined results from numerous different experimental runs (in fact, at 2 Atm.HCl, each point on the curve represents a separate run). Several

different amounts, moreover, of acid latex were prepared and used throughout these experiments.

5.2. Features of the Kinetic Curves and the Effects of Acid Concentration in the Serum.

The main features of the rate curves of Hevea latex hydrochlorination can be observed as

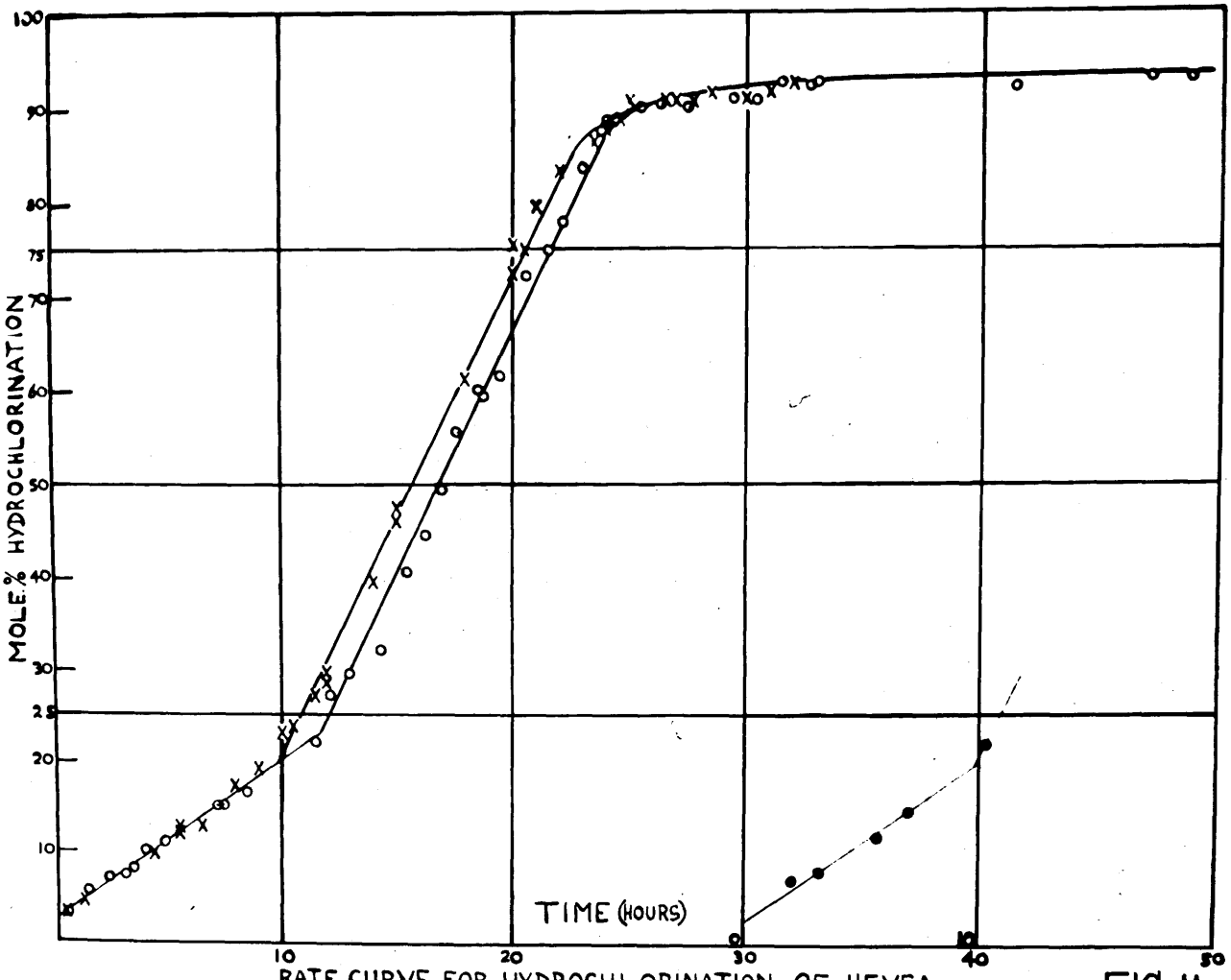
1) a small initial "jump", i.e. the fast hydrochlorination of a small percentage (.5 to 5) of isoprene units. This initial abnormality was later identified (when synthetic polyisoprene latex hydrochlorination was being studied) as a surface reaction (Chapter 8).

2) A linear portion of relatively slow zero-order rate, $k_1$. This retarded rate period is shown below to be due to the presence, within the rubber particles, of a basic retarding substance.

3) A "kink" at which the retarded rate portion changes sharply to another linear portion of fast zero-order rate $k_2$ which covers the main part (60% or more) of the total reaction.

4) A rapid decrease in rate as the hydrochlorination comes to a standstill well before stoichiometric completion.

This general pattern is repeated over a 70-fold variation in the main rate $k_2$ achieved through changes in pressure and temperature.

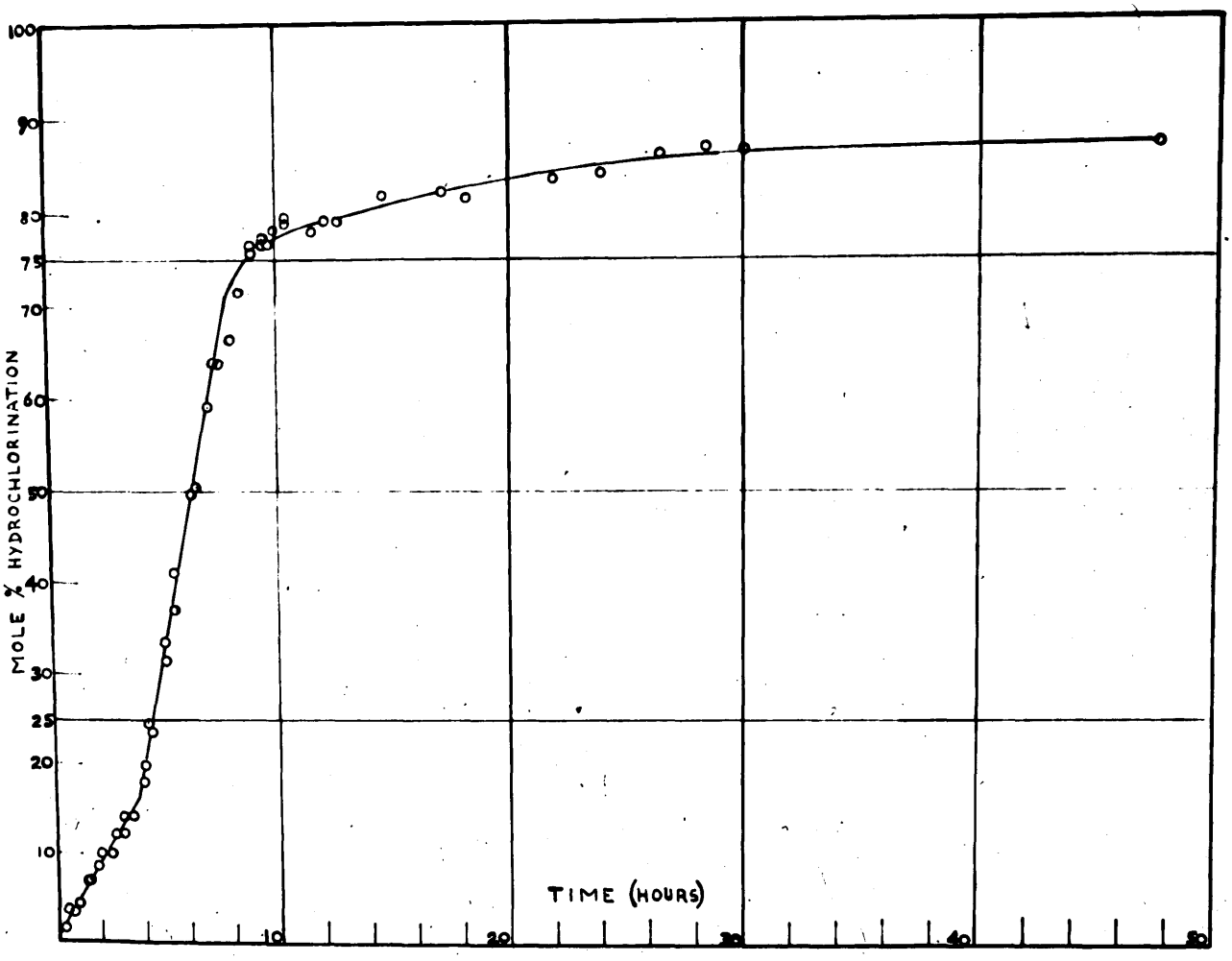



RATE CURVE FOR HYDROCHLORINATION OF HEVEA LATEX AT 26·7°C AND 1 ATM. OF HCl.

FIG. 16

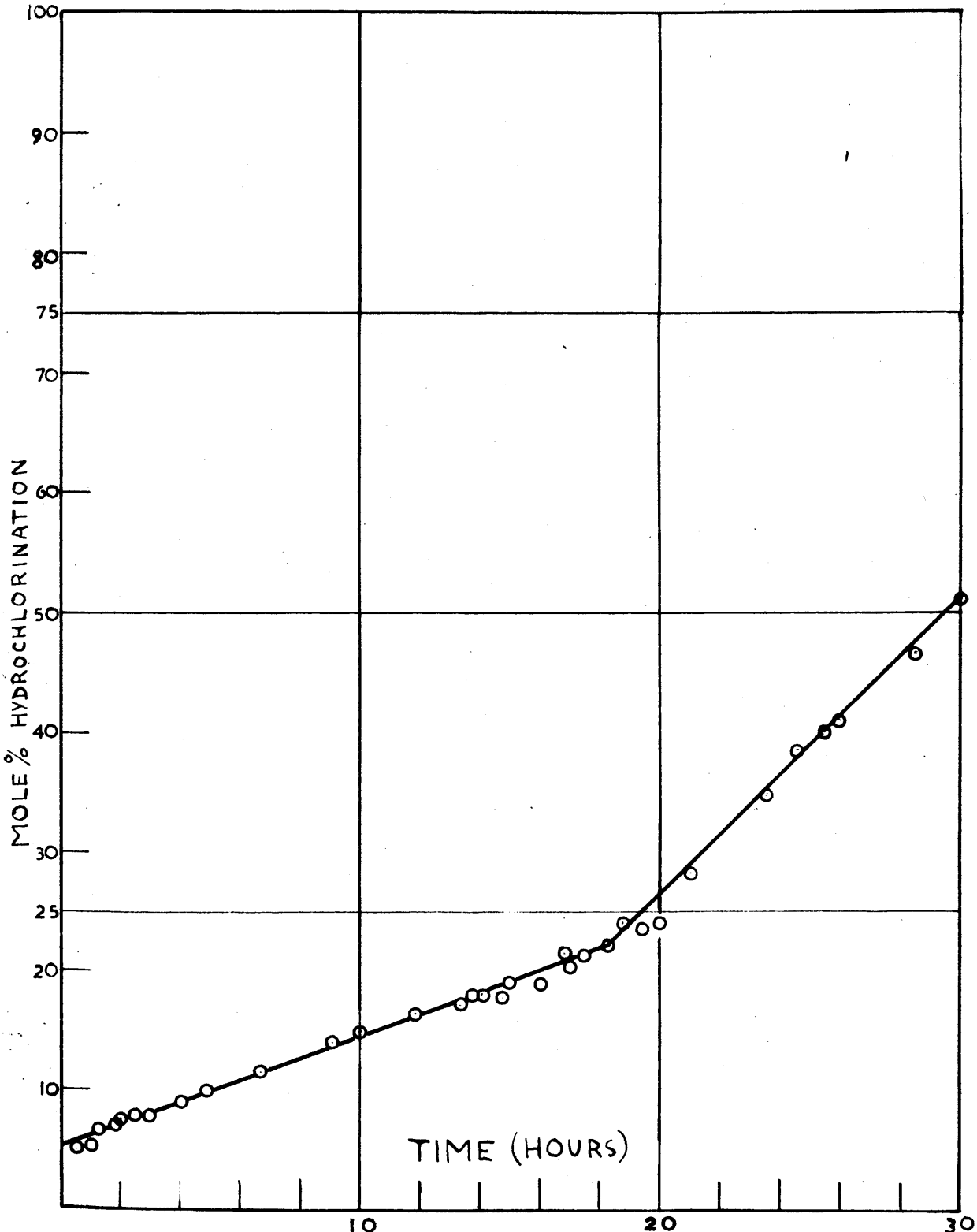
× SAMPLES FROM LATEX BATCHES WHICH PRODUCED SHORTER RETARDED RATE ($R_1$) PERIOD.

● INSET DIAGRAM SHOWS THAT RATE IS UNAFFECTED BY STOPPING AND RESTARTING THE REACTION.




RATE CURVE FOR HYDROCHLORINATION OF HEVEA LATEX AT 0°C AND 1 ATM. OF HCl.

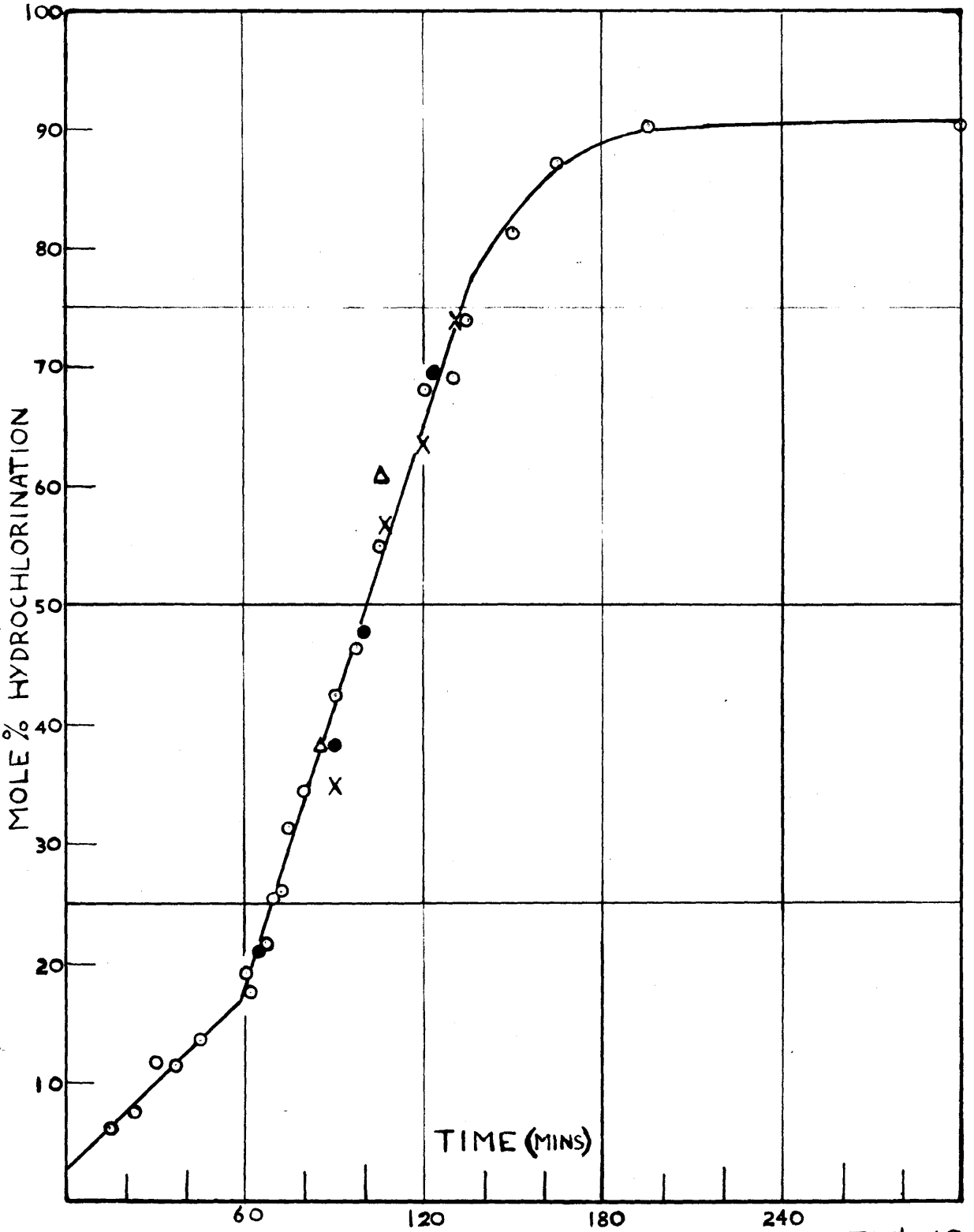
FIG 17




RATE CURVE FOR HYDROCHLORINATION OF HEVEA LATEX AT 69·5 °C AND 0·91 ATM. HCl

(MECHANICAL COAGULATION PREVENTED REACTION BEYOND 51 MOLE%)

FIG 18.



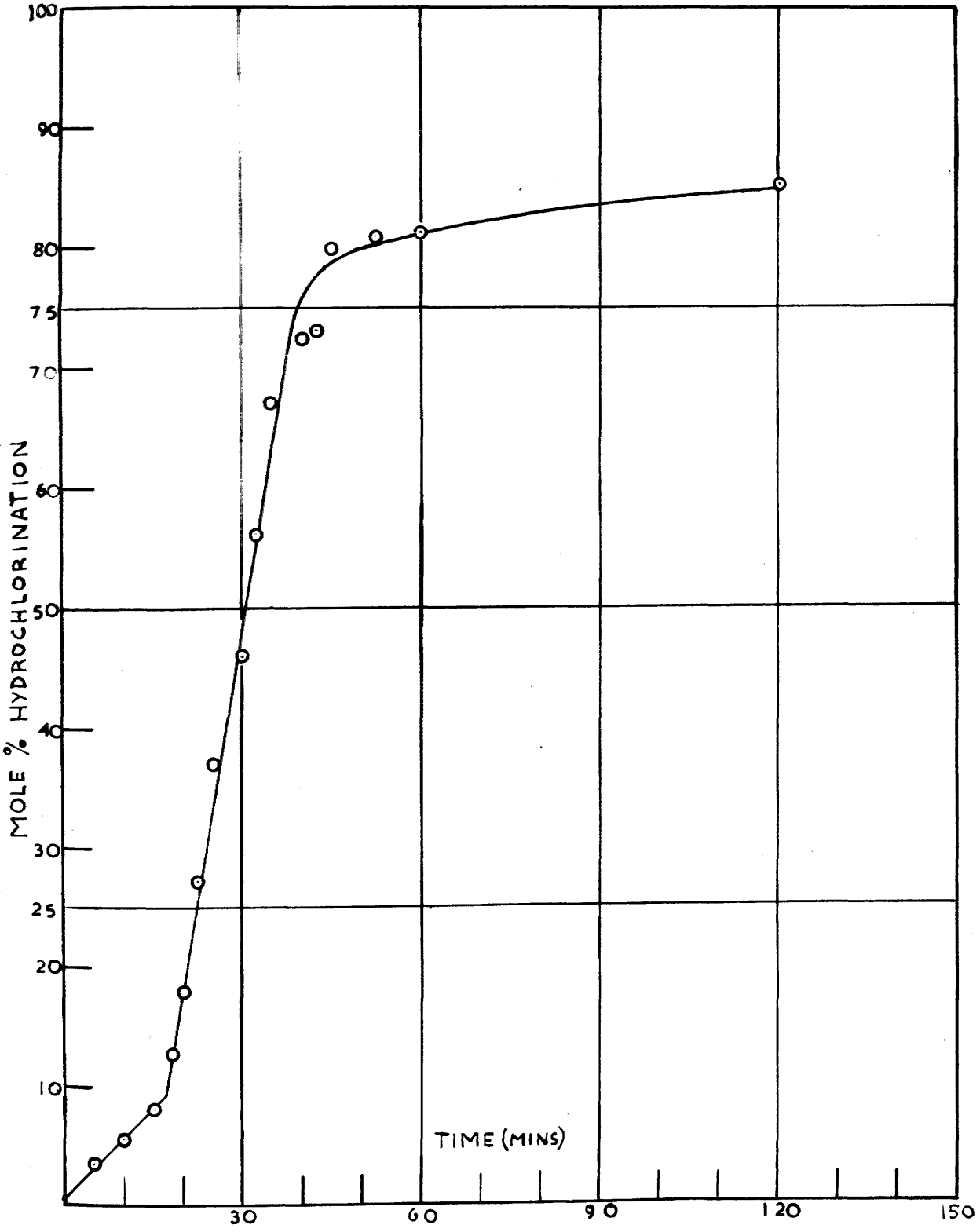

RATE CURVE FOR HYDROCHLORINATION OF HEVEA LATICES AT 26·7°C AND 2ATM. HCl. FIG. 19

O···· NORMAL STABILIZED DUNLOP LATEX (1·5% VULCASTAB L.W. ON DRY RUBBER)

X····ADDITIONAL STABILIZER (4·5% VULCASTAB L.W. ON DRY RUBBER)

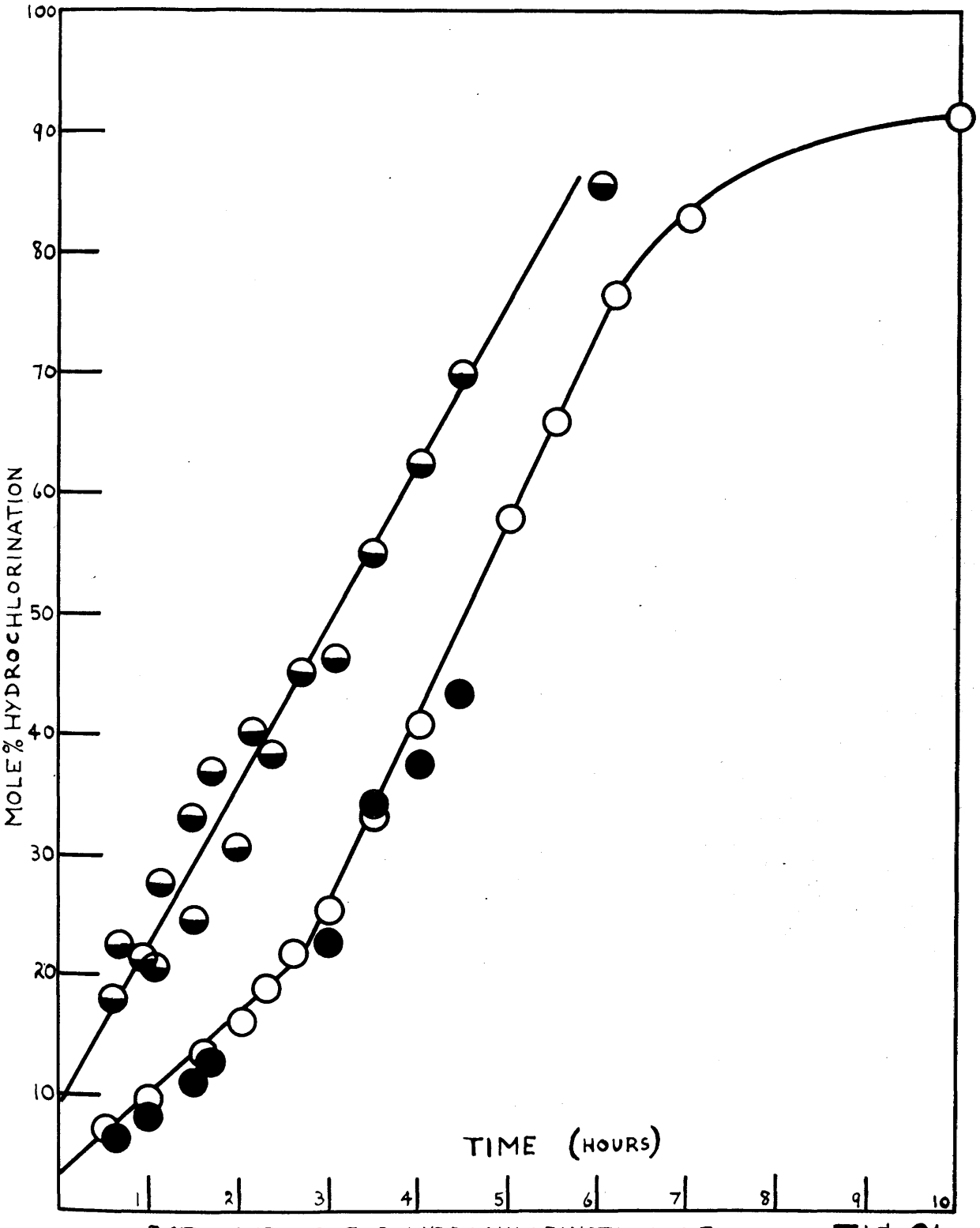
●····CREAMED DUNLOP LATEX (24 HRS UNDER ALKALINE CONDITIONS)

Δ····STANDARD REVERTEX (1·5% VULCASTAB L.W. ON DRY RUBBER)




RATE CURVE FOR HYDROCHLORINATION OF HEVEA LATEX AT 0°C AND 2 ATM. HCl.

FIG. 20




RATE CURVES FOR HYDROCHLORINATION OF HEVEA LATICES AT 69.5°C AND 1.95 ATM. OF HCl, AND INFLUENCE OF PARTICLE SIZE ON THE RATE.

FIG. 21.

O····WHOLE LATEX ◒····FINE FRACTION (F)

●····COARSE FRACTION (C)

At constant pressure the hydrochlorination rate decreases with temperature, and at constant temperature the rate increases rapidly with pressure.

The effect of the concentration of hydrogen chloride in the latex serum on the rate of reaction is observed by noting that the main rate $k_2$ is increased 6-14-fold in going from 1 to 2 Atm. (69.5 - 0°C range in temperature). Since the equilibrium concentration of hydrogen chloride in the serum varies by only a few per cent (not more than 2) at these two pressures (at a given temperature), the enormous sensitivity of the rate to acid concentration is demonstrated. This is paralleled by the sensitivity of the rate of rubber cyclization to sulphuric acid concentration. In this reaction, Gordon (12) was able to correlate the rates with a Hammett acidity function ($H_o$).

Table 4 below illustrates the variation of hydrochlorination rate with acid concentration in the latex serum, and summarizes the features of the rate curves (Fig.16-21) .

TABLE 4

| Temperature (°C). | 0 | | 26.7 | | 69.5 | |
|---|---|---|---|---|---|---|
| HCl Pressure (Atm). | 1 | 2 | 1 | 2 | * 0.91 | * 1.95 |
| % HCl in Serum. | 45.50 | 47.00 | 40.70 | 42.70 | 34.00 | 35.80 |
| Main rate $k_2$ (Mole.%/hr). | 12.50 | 181.00 | 5.20 | 47.50 | 2.50 | 15.50 |
| Retarded rate $k_1$ (Mole.%/hr). | 4.10 | 30.00 | 1.80 | 14.50 | 0.90 | 6.50 |
| Initial "jump" (Mole.%). | 0.75 | 0.50 | 2.50 | 2.00 | 5.50 | 3.00 |
| $k_1/k_2$. | 3.00 | 6.00 | 3.00 | 3.30 | 2.70 | 2.40 |
| % reaction at "kink" (Mole.%). | 16.50 | 9.30 | 20.00<br>22.80 | )17.00 | 22.00 | 21.00 |

* Computed by interpolation from International Critical Tables, through subtraction of the equilibrium water vapour pressure.

---

The complicating temperature effects prevent any simple or straightforward correlation of hydrochlorinat--ion rate measurements with hydrogen chloride concentration in the serum.

The rate-controlling step in latex hydrochlorination is interpreted (See Chapter 9) as the formation, within the polymer particle, of an ion pair ($H^+$,$Cl^-$) from ionic precursors ($H^+$ and $Cl^-$). The proton is probably solvated as $H_2Cl^+$ and the precursors are in diffusive

equilibrium with the aqueous, and hence the vapour phase. The concentration of $H_2Cl^+$ is likely to be governed by some Hammett acidity function (probably $H_o$). Hammett (28) originally defined the function in connection with indicator equilibria, but it is also known that in numerous reactions which proceed via the conversion of a base substrate to its conjugate carbonium ion, Hammett functions represent the variation with acid concentration of rate constants.

Unfortunately, Hammett acidity functions in HCl solutions are known only at low HCl concentrations, but work is now proceding in this College to extend the acidity function measurements to the HCl concentrations required for latex hydrochlorination, and when these data become available some correlation with the observed rate-measurements may be possible.

The temperature effect, a decrease in rate with rising temperature (negative apparent activation energy), is generally ascribed to a pre-equilibrium producing reaction precursors exothermally and reducing their concentration (or activity). It may be possible to find a relationship between rate constants and activity-product measurements of $a_{H^+}a_{Cl^-}$, but again, knowledge of ion activities is limited to the more dilute HCl solutions, and the temperature effect is complicated. In this respect,

Harned and Seltz (29) were able to relate ionic activity-products ($a_{H^+}a_{Cl^-}$) to kinetic rate constants for the conversion of acetyl-chloro-amino-benzene to p-chloro-acetanilide (up to Molar HCl).

5.3. Apparent Energy of Activation

The apparent energy of activation at constant HCl pressure is an appreciable negative quantity. The Arrhenius plots are not linear, the negative value of the apparent activation energy decreasing with temperature. The conventional equation

$$E = \frac{R.Ta.Tb.\ \log_e(k_b/k_a)}{T_b - T_a}$$

was used to evaluate E, the rate constants referring to the respective main rates of hydrochlorination $k_2$

TABLE 5

| Temperature Range | 0 - 26.7°C | 26.7 - 69.5°C | 0 - 69.5°C |
|---|---|---|---|
| E (1Atm.) (k.cals) | - 5.32 | - 3.60 | - 4.36 |
| E (2Atm.) (k.cals) | - 8.00 | - 5.36 | - 6.58 |

The explanation for such a negative value of E has been given above, and the discussion in Chapter 9 proposes equilibrium effects which reduce the true activation energy to the apparent activation energy.

5.4. Freedom of the Measured Rate of Latex Hydrochlorination from Chance Effects

5.4.1. Rate of Stirring

The rate of latex hydrochlorination was

not expected to be affected by the rate of stirring, provided this exceeded a certain minimum which maintained therate of HCl absorption from gas to liquid. This was confirmed by obtaining identical kinetic results when the stirring rate was varied over a wide range (30-120 r.p.m. at 26.7°C, 2 Atm.HCl), and also when two different modes of stirring were employed (Section 4.4.3.) . At reaction rates approaching 200 Mole.% per hour ($k_2$ at 0°C, 2 Atm HCl) stirring effects became difficult to avoid, and the fast minimum stirring rate required to maintain absorption began to cause mechanical coagulation after longer reaction periods. Mechanical coagulation of the latex also prevented kinetic measurements beyond 50 Mole.% conversion (30 hours) being made at 69.5°C, 0.91 Atm. HCl,even although only slow stirring was required. Transport control of the measured reaction rates seems intrinsically unlikely, the shape of the kinetic curves being characteristic rather of chemical rate-control.

5.4.2. Concentration of Serum Constituents

The presence of the slow steady rate $k_1$ and its sudden change to the main rate $k_2$ seem to signify the presence of some retarding substance in the latex system. The following experiments were undertaken at 26.7°C, 2 Atm HCl in an effort to try to determine the presence and locus of a retarder.

Some Hevea latex was creamed so that the serum constituents, and constituents adsorbed on the rubber particles in sufficiently mobile equilibrium, were reduced to less than one-fifth in concentration. The cream was then acidified and hydrochlorinated, and the experimental points are shown by full circles on Fig. 19, and lie close to the curve for uncreamed latex.

Standard Revertex (75% rubber content),which is concentrated by evaporation rather than centrifuging, and which has a high serum solids concentration was also hydrochlorinated, and provided experimental points (squares on Fig.19) lying close to the normal rate curve. This, moreover, demonstrated the reproducibility of hydrochlorination rate of latex from different plantations.

Finally, the non-ionic stabilizer(Vulcastab L.W.), the most important solute in the serum (and on the particle surface),was shown to have no influence on the rate, since a 3-fold increase in its normal concentration provided experimental points (crosses on Fig. 19) which again do not deviate from the normal kinetic curve.

These three experiments , showing that the rate is unaffected by changes in the concentration of serum constituents, implied that if a retarding substance is present in the latex system, it must be located within the rubber particles themselves. This concept was suppor-

-ted and finally proved by the pieces of evidence and experiment reported below in Section 5.5.

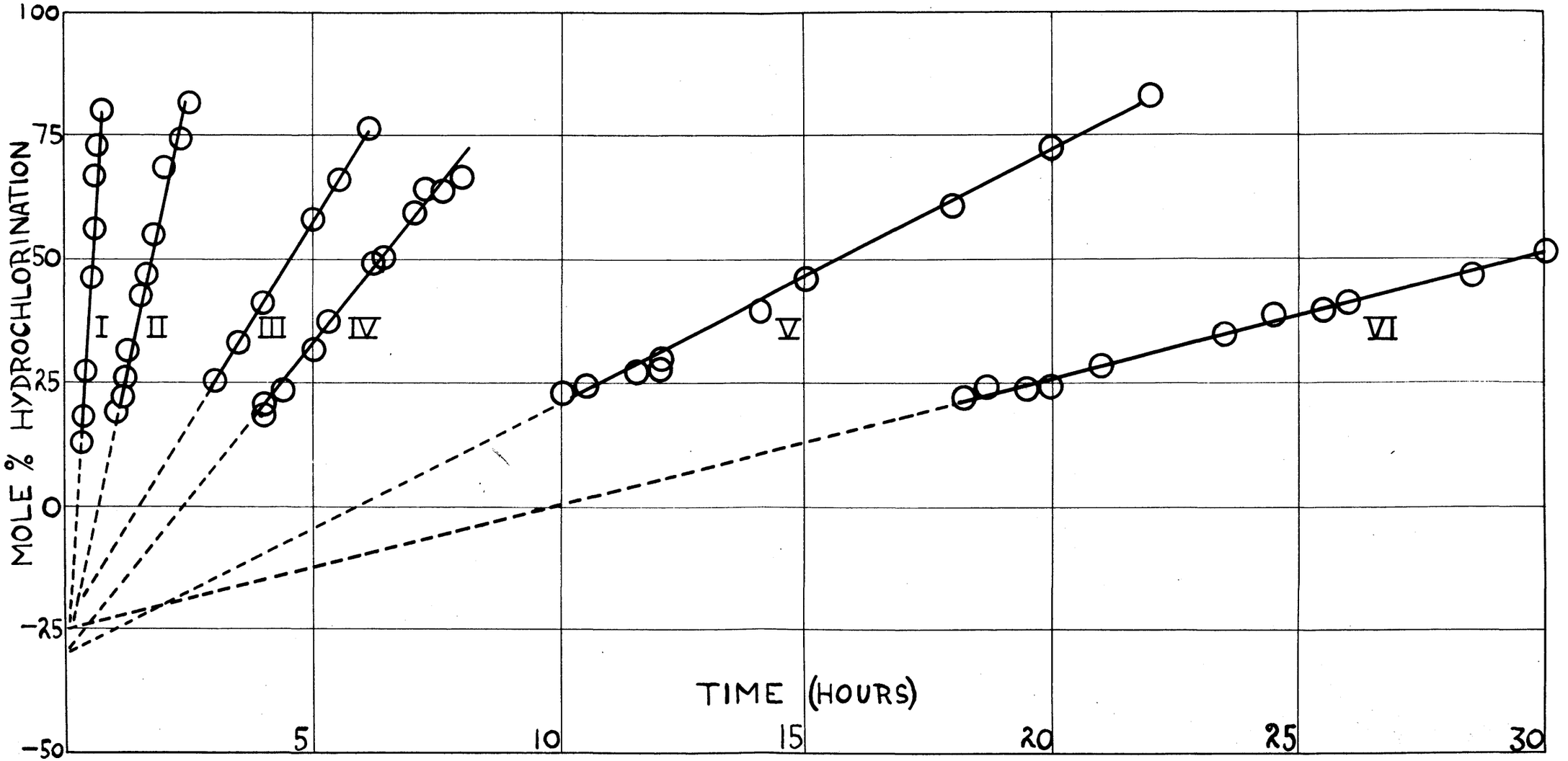
## 5.5. Evidence For Hydrochlorination Retarder Within The Hevea Latex Particles

Two lines on Fig. 16 are drawn to represent the main rate $k_2$ of hydrochlorination at 26.7°C, 2 Atm.HCl. These lines are parallel and their linearity is established. The"advanced"line became apparent after run 1Q. (When the drum of latex was about 8 months old), i.e. in the hydrochlorination runs (represented by crosses) after 1Q, the main rate $k_2$ took over sooner from the retarded rate $k_1$. No explanation for this is apparent because several points on each line represent results from the same batch of acid latex, the experimental conditions were not changed, and chance effects have been shown to have no influence on the rate. The decrease in the retarded rate period of the reactionat 26.7°C,1Atm. HCl (11.5 to 10 hours) appears to indicate a sudden change in amount of retarder present. It is difficult to see any reason for this, because the retarder is thought to be basic and yet the irregularity was observed with latex which had been stored under both acid and alkaline conditions. The anomaly was not repeated or observed under different experimental conditions.

When synthetic polyisoprene latices are hydrochlorinated, the retarded rate period is entirely

missing (Chapter 8). This confirms that the effect is not an essential part of the hydrochlorination mechanism, and lends support to the suggestion that a special retarding substance is present inside the natural latex particle.

A further piece of evidence for this concept is presented from Fig.22, where rate curves are plotted for Hevea latex hydrochlorination under six different conditions of temperature and HCl pressure. Only the main line of slope $k_2$ is drawn in each case and extrapolated back to zero time as a broken line . For simplicity, the experimental points related to the earlier parts of the reactions (the linear portions with slope $k_1$) have been omitted. The extrapolated lines converge to $-27\pm3$ mole% hydrochlorination. This kinetic observation implies that when the retarded reaction is completed and the full rate $k_2$ takes control, 27% of the rubber units present have escaped reaction. In an unretarded system (e.g. furnished by synthetic latex), this is the additional amount of hydrochlorination observed to have taken place in the bulk of the particles in that time. The hypothesis that retardation is associated with a material agent inside the particles is thus supported, because for this hypothesis the law may be stated that the retarder deactivates a constant weight of reactive hydrogen chloride species ($H^+$,$Cl^-$) irrespective of the temperature, pressure, and




EXTRAPOLATION OF MAIN RATE ($k_2$) OF HEVEA LATEX HYDROCHLORINATION TO COMPOSITION AXIS

FIG. 22.

I HEVEA LATEX AT 0°C, 2 ATM. HCl.
II " " " 26·7°C, 2 ATM. HCl
III " " " 69·5°C, 1·95 ATM. HCl
IV HEVEA LATEX AT 0°C, 1 ATM. HCl.
V " " " 26·7°C, 1 ATM. HCl.
VI " " " 69·5°C, 0·91 ATM. HCl

and reaction rate. This constant weight is, however, far too large to reflect merely a stoichiometric combination with the retarder. The retarder is present only in trace amounts, so that each molecule of this substance must account for a considerable but (on average) constant number of HCl species derived from hydrogen chloride. A chain reaction is therefore indicated, although many possible schemes arise. Retardation rather than complete inhibition is involved.

It has been shown above (Chapter 5.4.2.) that an attempt to reduce the retardation effect by creaming the latex under ammoniacal conditions was completely unsuccessful. On the assumption that the retarder is likely to be a basic substance inside the particles, one was led to the expectation that extraction of the finest available particles with acid would furnish the most favourable conditions for such a reduction. These conditions apply during differential creaming over extended periods from serum containing approximately 10% HCl.

Fig.21 illustrates plots for the hydrochlorination at 1.95 Atm HCl, 69.5°C of normal Hevea latex (open circles), fine fraction (F) of acid creamed latex (half circles), and coarse fraction (C) of acid creamed latex (full circles). It can be seen that the fine fraction

(F) was indeed free from the retardation effect (only rate $k_2$ apparent), and the presence of a retarding substance in the unextracted particles can hardly be doubted. The detailed characterization of the structure and mode of action of the retarder remain unsolved, and would be a matter of much biological and technical interest.

The increased intercept on the composition axis for fraction (F), and the decreased intercept for fraction(C), reflect a change in the extent of the initial rate abnormality and constitute proof that the abnormality is due to a surface hydrochlorination reaction (see Chapter 8 for full discussion and identification of this effect).

It was, in fact, in this latter connection that Mr. C. Moss (Dunlop Rubber Co.) suggested selective creaming as a means of obtaining fractions of different particle size from natural latex, but it will be convenient to give the experimental details at this point.

40 gms of Dunlop 60% Hevea latex were compounded with 1.8 gms of a 20% aqueous solution of Vulcastab L.W. and 40ccs of concentrated hydrochloric acid. To this were added 200ccs of a 0.07% aqueous solution of ammonium alginate. The latex was then filtered through fine-mesh glass cloth and allowed to stand for two months in a separating funnel. After this period , the bottom 10ccs of clear serum were run off, and the

next 40ccs were taken for fraction (F). The top 20ccs of the cream were taken for fraction (C).

The dispersion (F) contained only 1.2% solids (initial density $d_o$=0.9080), and each of the experimental points on the hydrochlorination of this fraction was performed on roughly 1-2 mgm of rubber dispersed in about 150 mgms of aqueous hydrochloric acid. The unusually high scatter of the points is attributable to these unfavourable conditions. The coarse fraction (C), of solids content 59% ($d_o$=0.9024), was hydrochlorinated without further dilution, but mechanical coagulation (at 69.5°C) prevented samples of greater than 43.5 mole.% hydrochlorination being obtained. The varying values of $d_o$ were allowed for when interpolating mole.% conversion.

For the points (full circles) on the rate curve shown in Fig.19, the Hevea latex was creamed as above but without previous acidification, and was left to cream for only 24 hours. The top cream(solids content 50%) was taken for acidification and hydrochlorination.

## 5.6. Effect of Stopping and Restarting Hevea Latex Hydrochlorination.

It was shown by experiment that latex hydrochlorination could be stopped and restarted without interfering with the course of the reaction. This was achieved by hydrochlorinating the latex at 1 Atm. HCl, 26.7°C for two hours. The reaction was then halted by

by diluting the latex 6-fold with cold distilled water. A sample was then taken for analysis, and after 24 hours storage another sample was taken from the diluted latex. As expected, the densities of these two samples were identical. The reaction was then restarted and samples were withdrawn after various time intervals. These results are shown in the inset (full circles) in Fig. 16, and lie very close to the normal rate curve (full line). The maximum attainable conversion was not affected either.

Tables of experimental results for the graphical Figures in this chapter are given in the appendix (Tables 6-14).

5.7. Examination for Reversibility in Latex Hydrochlorination.

It was claimed by van Veersen that a maximum conversion of 98.7 mole.% could be obtained in the latex reaction (17). The maximum conversion observed in the writer's work was 93.5 mole%, achieved with ease at 26.7°C. It was however noted that at 0°C the extent of the reaction could be raised to 89 mole.% only with difficulty (60 hours, Fig. 17). This gave rise to the suspicion that some reversibility existed, and the following experiments were carried out to test for this.

Run 2L The latex was reacted for 22 hours at 0°C, 1 Atm. HCl and conversion carried to 83.5 mole% (sample 2L.1). It was then put under slight vacuum and

allowed to warm up to 26.7°C. The reaction was then restarted and samples were taken at intervals.

Table 15

| Sample No. | 2L.2 | 2L.3 | 2L.4 | 2L.5 | 2L.6 | 2L.7 | 2L.8 |
|---|---|---|---|---|---|---|---|
| Time after Restarting. | 30m | 1hr 20m | 3hr 20m | 4hr 35m | 5hr 35m | 6hr 15m | 12hr 30m |
| Mole% reaction. | 84.5 | 85.5 | 88.6 | 90.0 | 90.0 | 90.5 | 91.2 |

Table 15 shows that the isoprene units left unreacted at 0°C were still available for reaction.

After 2L.8, the latex and the acid in the bubbler of the reactor (Fig.15) were resaturated, at atmospheric pressure and 0°C, with HCl, and the reaction was again started.

Table 16

| Sample No. | 2L.9. | 2L.10 | 2L.11 | 2L12 | 2L.13 | 2L.14 | 2L.15 |
|---|---|---|---|---|---|---|---|
| Time after Restarting. | 15m | 50m | 1hr 20m | 4hr 20m | 5hr 20m | 23hr 20m | 46hr 20m |
| Mole.%reaction. | 91.0 | 90.0 | 90.0 | 90.4 | 90.0 | 90.5 | 90.5 |

These results give no evidence of reversibility.

Run 2M The initial approach was then made from the other direction. Latex was hydrochlorinated at 26.7°C, 1Atm. HCl tothe extent of 91.5 mole.% conversion(Sample 2M.1). It was then cooled to 0°C and the reaction was restarted.

It can be seen that no decrease in percentage hydrochlorination was observed (table 17), and once more no evidence for reversibility was obtained.

Table 17

| Sample No. | 2M.2 | 2M.3 | 2M.4 | 2M.5 | 2M.6 | 2M.7 |
|---|---|---|---|---|---|---|
| Time after Restarting. | 15m | 2hr | 3hr 15m | 4hr | 5hr 15m | 25hr 20m |
| Mole% reaction. | 91.25 | 92.0 | 92.75 | 92.75 | 92.0 | 93.0 |

The most likely explanation for the difficulty in obtaining high conversions at 0°C is that crystal formation in the polymer "protects" unreacted units from the reactive hydrogen chloride species which have difficulty in reaching them (see also Chapter 8.2.)

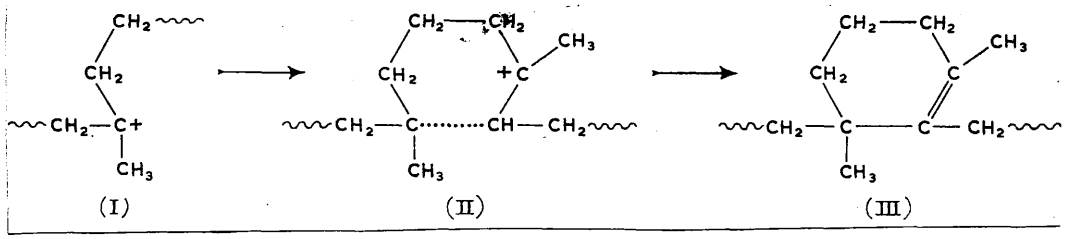
Even at 69.5°C, however, stoichiometric completion was far from being attained. A cyclization side reaction has been suggested as the cause of incomplete conversion in hydrochlorinating rubber solutions (4), and although van Veersen claimed its absence in the latex reaction, he later reported (30) that hydrochlorinated rubber can be directly converted to cyclized rubber by acid catalysis at elevated temperatures. This suggests that cyclized rubber and hydrochlorinated rubber may go through the same intermediate.

--------ooOoo--------

# CHAPTER 6

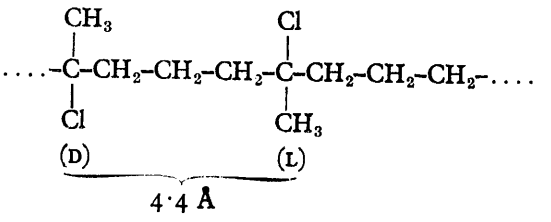
## Proposed Stereodynamic Course of Chain Reaction for Hevea Rubber Hydrochlorination

The ionic reaction of rubber cyclization was shown by Gordon (12) (31) (32) to be of a co-operative nature in the sense that adjacent isoprene units are involved together. This feature is due to the 1:5-unsaturated structure of rubber. The cyclization proceeds by the acid catalytic "protonation" of an isoprene unit to the carbonium ion I, which immediately attacks its free neighbour to form a cyclic carbonium ion II. This cyclic ion then loses a proton in a slow rate-controlling step to form the stable cyclized rubber structure III, which was first deduced by D'Ianni et al. (15).




The following mechanistic theory of Hevea rubber hydrochlorination (introductory paper, Ref (65) ) is based on the detailed and accurate crystal-structure determination of rubber hydrochloride by Bunn and Garner (1). The reaction is proposed below to be an outstanding example of co-operation; whole sequences of isoprene units are concerned, three of them entering together into a common transition state.

Bunn and Garner reported that successive tetrasubstituted carbon atoms along a rubber hydrochloride chain segment lying in a crystal micelle are alternately antipodes, so that odd-numbered units along a particular chain segment may be designated as the D-structure, and even ones as the L-structure, thus:




The length of the crystals is estimated to be hundreds of Angstrom units, i.e. scores of isoprene units. For the growth of such crystals to be possible, alternating sequences (DLDLDL-----) comprising scores of isoprene hydrochloride units must frequently occur in the polymer chain. Bunn and Garner reported, "..... it appears that when an HCl molecule has added on to one double bond, the atomic grouping so formed has a directing influence on the process of addition to the next double bond ". This represents the chief clue to the chain mechanism for hydrochlorination propounded below.

The original rubber molecule is, of course, free from asymmetric centres. When the early stages of the reaction are considered it is seen that isoprene units cannot be converted into hydrochloride via carbonium ions formed <u>randomly</u> along the polymer chain.

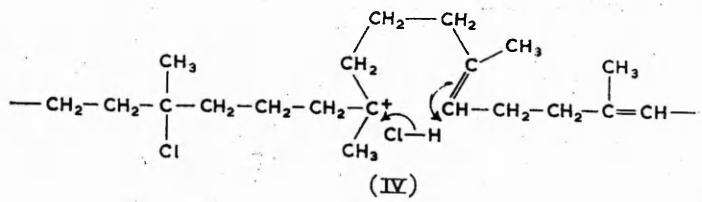
The correct acquisition of the D-form by an odd-numbered unit would have to be promoted, with almost unfailing precision, by asymmetric induction from a previously hydrochlorinated unit, separated from the point of reaction by numerous symmetric isoprene units. It is inconceivable that an asymmetric induction force can act with alternating effect across enormous distances along a wriggling polymer chain. The only alternative is that rubber hydrochlorination is a chain reaction, passing along the polymer chains from unit to unit like a zip-fastner (cf. acetic acid splitting off during polyvinyl acetate degradation (33)).

To express this in more precise kinetic terms, the repetitive propagation step, which must carry the hydrochlorination forward along the polymer chain, will be examined.

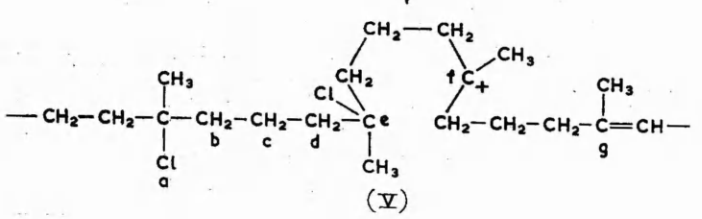
To ensure a kinetic chain-length of 50 or so successive isoprene units, uninterupted by a competing random-hydrochlorination process, it is necessary for any unit, adjacent to one that has previously reacted, to be several hundred times as reactive to hydrochlorination as one not so privileged. This excessive reactivity can hardly be due solely to the hydrochlorination of a given unit. It cannot be expected that the addition of hydrogen chloride to a double bond increases the addition rate of

another double bond, four carbon atoms distant, by such a large factor.

It is deduced therefore, that at the precise moment at which the first unit establishes its C-Cl bond (thus electing its D- or L- configuration), its adjacent unit becomes activated by a positive ionic charge to propagate the chain reaction. The electrical charge of the activated chain-carrier unit must be constant from one propagation step to the next, in order to preserve the reactivity. Therefore, whatever assumption is made about the charge type of the activated rubber unit, the hydrochloric acid must be added as a neutral entity of HCl. (This neutral entity, initially taken to be a neutral molecule, was later deduced (Chapter 9) to be an ion pair). The HCl must then add across two isoprene units at a time, leading to the transition state IV, in which the positive charge is seen to flow from e to f (seeV),thus activating f at the moment the C-Cl bond is formed on the preceding unit at e.



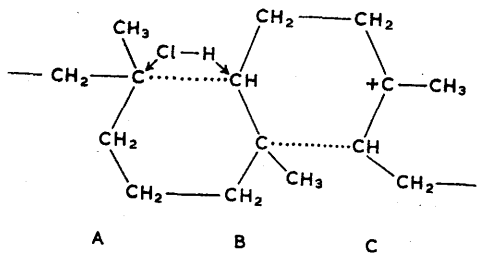
(IV)



(V)

This picture of the reaction, although an improvement, still suffers in a milder form from the original difficulty. It is still necessary to postulate an asymmetric induction acting across the three methylene groups b,c,d, to ensure that the asymmetric carbon atom just created at e in V has a structure antipodal to a. This still appears to be an excessive demand for the efficiency of asymmetric inductions across chains of $CH_2$ groups (34). Therefore it is not possible to allow the establishment of a planar carbonium ion (with only three bonds) at f at the moment at which e becomes tetrahedral by acquisition of the Cl. The two successive centres e and f must become stereochemically committed (i.e. tetrahedral) simultaneously. The centre f must acquire a fourth bond at the same time as e; to what atom is this fourth bond of f to be directed? The answer is not a chlorine atom because this merely shifts the whole induction problem along to the next isoprene unit g, and it is inconceivable that all the HCl molecules (ion pairs) add to a rubber chain by snapping into position simultaneously. Also, since the reaction can be carried out in aqueous emulsions and various dry solvents under different conditions, the fourth bond can hardly be directed to anything derived from the medium, water or solvent. Rubber itself is the constant factor, and the

carbonium ion at f must be attached as soon as it is formed, without letting it exist freely, to another isoprene unit of the rubber. Such an unit is generally available at g, and further, such an attachment is normally formed with great speed and ease as has been noted in the discussion given above of the cyclization reaction. The fourth bond of f is thus the weak bond that closes the ring in the cyclic ion II. The notion that rubber hydrochlorination and cyclization go through a common intermediate (cyclic ion) is supported by the fact that hydrochlorinated rubber can be directly converted by acid catalysis into cyclized rubber at elevated temperature (30). The transition state VI, which involves one neutral HCl entity and <u>three</u> <u>adjacent</u> isoprene units, has now emerged. The HCl no longer adds across a "gap" between two isoprene units as in IV, but across the weak bond of a cyclic ion, and as it thus breaks the bond between units A and B, a new ring of the same structure is formed between units B and C.



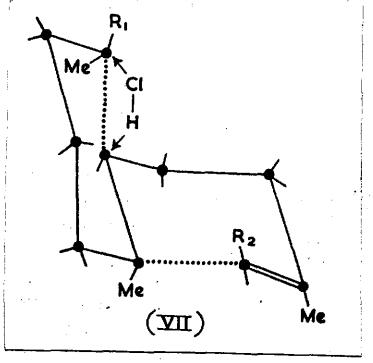

(VI)

The transition state VI seems necessary to account for the alternation of antipodes in hydrochlorinated rubber, but is it also sufficient? To answer this, one has to look into the stereochemistry of the fused-ring

structure of transition state V1, which evidently bears a close relationship to a substituted decalin. A reasonable assumption reduces the large number of apparently possible isomeric arrangements. It is generally accepted that cyclo-hexane exists in the "chair" form (35), and the same is true of the rings in cis-decalin; also in trans-decalin where the bonds common to both rings are the "equatorial" type (36). As a working hypothesis, one may attempt to fit the decalin transition state V1 to these accepted cis- and trans-decalin structures. Since rubber is cis-polyisoprene, it may be thought that only cis-decalin comes into consideration; but when the double bond is temporarily opened up to the carbonium ion, inversion might occur in the transition state, thus leading to the trans-structure.

The stereochemistry of the postulated transition state V1 should show sufficient cause for the observation of alternating antipodes in the finished rubber hydrochloride. The alternation of antipodal quaternary carbons after addition of hydrogen chloride is inevitable provided that the two rings (i.e. the two successive chain-carriers), one of which is just breaking while the otheris just making in V1, have the same overall structure (and thus the same reactivity) and are themselves mirror images of each other. This is unaffected by whether

or not Walden inversion takes place in the formation of the C-Cl bond; this question was left out of consideration for simplicity.

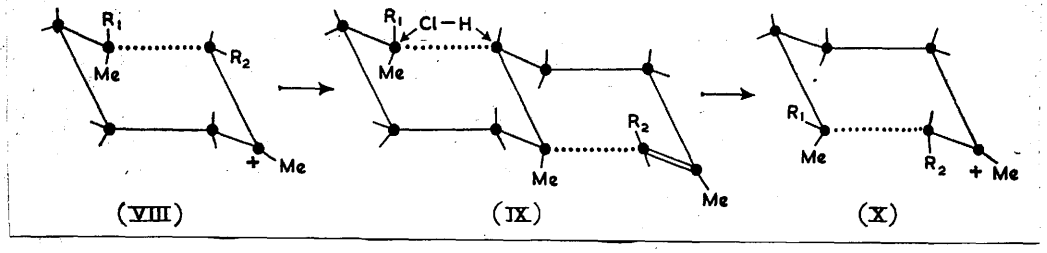



(VII)

Configuration VII presents the attempt to fit transition state VI to the structure of cis-decalin (36). Inspection shows that the two ring moities are not, in their free states, mirror images (see VIII-X below), nor even of identical structure. They would, in principle, vary in reactivity (rate of hydrochlorination), though it appears that they would give alternating antipodes if the transition state could be achieved in this way. Ball models quite plainly show that this is not so because of strong steric interference of two substituents, namely the hydrochlorinated rubber chain $R_1$ and the as yet unchanged rubber chain $R_2$.

The application of VI to the accepted trans-decalin structure (36) is shown in three stages, VIII to X; IX is the transition state proper. The two successive rings VIII and X, of which the former is breaking and the latter making in IX, are true mirror image twins

of equal reactivity, which will inevitably lead to the required alternation of antipodes. Ball models show that IX can be achieved with relative ease, especially since some increased flexibility should accrue from the simultaneous breaking of one of the rings. It can be seen fromthe positions of $R_2$ in IX and X respectively that the result depends on the inversion of the cis-isoprene unit.




It has been shown therefore, that the fact of alternating antipodes leads directly to the notion of a chain reaction with a transition state such as VI, and conversely, that the assumption of the existence of VI leads to the possibility of alternating enantiomorphs.

Bunn and Garner's X-ray structure analysis was carried out on a sample with 20% of the units unhydrochlorinated. They could not lie scattered randomly among those that had reacted, as that would have prevented crystallization. They must lie in relatively long sequences in the amorphous regions. This supports the block-copolymer structure and the chain mechanism envisaged above.

Co-operative reactions are important because (as in the cyclization reaction) they may reveal

the structure of the units present, their environment of neighbouring units, and yield information as to the flexibility, coiling, and internal molecular dynamics of the polymer chain. However, the chemical co-operative or stereodynamic effects of the organic polymer in the hydrochlorination reaction are lost to us because they take place at a high speed immediately after the purely inorganic rate- controlling step (which is deduced in Chapter 9). It will be seen later however that the simplicity of the rate control has its compensations in illuminating colloid chemical aspects.

The hydrochlorination of balata, which is the trans-isomer of rubber, leads to a product that is not crystalline and consequently not likely to possess a substantial proportion of long sequences of alternating antipodes. If inversion to the cis-ring-structure occurs with balata, analogously with the deduced inversion of rubber to the trans-ring-structure, a ball model shows that the cis-decalin-like transition state cannot be achieved owing to steric hindrance similar to that discussed above in connection with VII. Consequently, the reaction may occur by random conversion of isoprene units with hydrogen chloride which would account for the amorphous nature of the product.

It is noted that Bunn's X-ray diffraction

work on polyvinyl alcohol and copolymers of vinyl alcohol and ethylene (37) (38) (39) has shown that crystallinity can occur in chemically regular polymers although the substituent groups are stereochemically irregular, provided there is little difference in the size of the groups attached to the same chain atom. Thus if the right- and left-handed groupings in natural rubber hydrochloride were randomly distributed, crystallization could possibly still occur because of the comparative sizes of the Cl and $CH_3$ groups. This however would leave no explanation for the amorphous nature of balata hydrochloride since balata itself is chemically regular. In any case, Bunn and Garner's X-ray results on rubber hydrochloride are definitely in good agreement with sequences of alternating antipodes in the polymer crystal.

The hydrochloride of synthetic polyisoprene is also known to be amorphous. The crystallinity of natural rubber hydrochloride has been traced to the stereochemistry inherent in the long sequences of cis-isoprene units existing in the original rubber. Since such sequences are not eminent in synthetic polyisoprene, where 1:2- and 3:4-addition and geometric isomerism impair any semblance of regularity, the lack of crystallinity in the hydrochloride is explained. This comparison is further discussed in Chapters 7 and 9.

Obviously a complementary line of research in the field of degradative studies is indicated. It follows from the postulated chain reaction that long sequences of hydrochlorinated units should be capable of isolation from lightly hydrochlorinated rubber ( analogous to the attainment of high molecular weights by lightly chain-polymerized vinyl polymers as distinct from those randomly polycondensed). Preliminary work along these lines, carried out in this College by Mr.B.Grievseson, has been unsuccessful owing to the weakness of the C-Cl bonds apparent under degradative oxidation conditions. It would be of value to follow up this study, not only to credit the above chain reaction, but also in view of the current interest in "block-copolymers".

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# CHAPTER 7

## Synthetic Polyisoprene as a Different Substrate in the Hydrochlorination Reaction

Natural rubber consists of long sequences of cis-units in 1:4-addition (40-46). Synthetic polyisoprene has a different detailed chemical structure. D'Ianni (16) found that only 88-90% of the units in isoprene emulsion polymer were polymerized by 1:4-addition. 90% 1:4-addition in this type of polymer was reported by Gehmann et al.(43) from infra-red analysis. Therefore 10-12% of the units were likely to be in the 1:2- or 3:4-forms scattered along the polymer chain. Confirmation of this has been given by Richardson and Sacher (46) by their infra-red analysis of several persulphate-catalysed polyisoprene emulsions. In a typical case, they found 5% of 1:2- and 5% of 3:4-units, and further, that 72%of the units were in the trans - form and only 18% in the cis-form. It may be noted that trans-units predominate over cis-units in synthetic polybutadiene (47).

In the light of the above facts, synthetic polyisoprene may be considered as a different substrate from Hevea rubber in the hydrochlorination reaction. A change of substrate is the most stringent test for non-participation of the substrate in the rate control of a reaction. For instance, Hughes, Ingold and Reed (48), who applied the test in the field of reactions of organic

substrates with inorganic acids, showed that zero-order nitration was controlled by the rate of the reaction $O_2N\text{-}OH \longrightarrow O_2N^+ + OH^-$ .

Synthetic latices may be prepared free from the contaminants present in natural rubber latex. It was decided that the preparation of synthetic polyisoprene latices and a study of their hydrochlorination kinetics would greatly help in the elucidation of the mechanism of rubber latex hydrochlorination.

It may be noted here that one of the author's synthetic polyisoprene latices (No.III) was analysed by infra-red technique through the courtesy of Mr. W.H. Davison and the Dunlop Rubber Co. The result of this analysis was in substantial agreement with Richardson and Sacher (46).

% 1:2-addition units = 6.4 ± 0.3

% 3:4-addition units = 6.7 ± 0.3

% 1:4-addition units = 86.0 ± 4.0

The cis/trans fraction was not evaluated.

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CHAPTER 8

## Kinetics of Synthetic Polyisoprene Latex Hydrochlorination: Comparisons with Natural Latex Reaction

### 8.0. Review

The preliminary experiments on the hydrochlorination of synthetic polyisoprene latex were carried out by Mr.E. Crampsey (for B.Sc. Thesis) with co-operation from the writer. These entailed the hydrochlorination of synthetic latices I and II, and chlorine analyses of several samples for the calibration of per-centage hydrochlorination against specific volume. The micro-reactor described in Chapter 4.4.4. was employed for this work, and as before, the reaction progress was followed by density measurements. The potentiometric titration method was again used for chlorine analyses of the polymer. Acetone, instead of boiling water, was used to flocculate the latex samples which were then washed thoroughly, first with acetone, then distilled water and dried in vacuum.

The results of this early work, illustrated in Figs. 23, 24, and 25 (taken from the subsequent paper by Crampsey, Gordon, and Taylor (49)), immediately produced exciting comparisons with Hevea latex hydrochlorination, and revealed the following significant conclusions:

FIG. 24 *Hydrochlorination kinetics of synthetic latex II at* 300° K *and* 1 *atm. of* HCl.

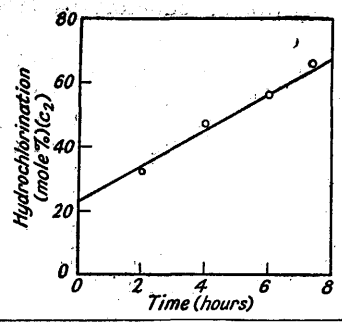
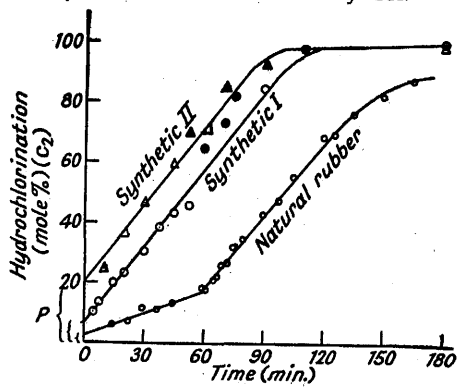
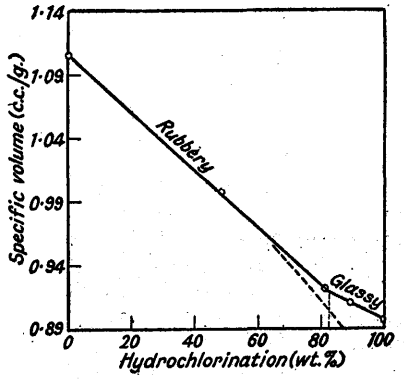



FIG. 23 *Hydrochlorination kinetics of polyisoprenes at* 300° K *and* 2 *atm. of* HCl.




*Full circles and full triangles : after prolonged storage.*

FIG. 25 *Specific volume as function of composition of polymer.*




——— *Synthetic latex I.*
– – – – *Natural latex.*

1) the initial abnormality (which was observed in natural latex as the fast hydrochlorination of a small % of isoprene units) is greatly increased in synthetic latex, and its extent found to be dependent on the particle size of the polymer in the latex.

2) The retarded rate is entirely missing in synthetic polyisoprene hydrochlorination.

3) The main zero-order rate ($k_2$) of the reaction is almost identical for both synthetic and natural polyisoprene hydrochlorination under the same experimental conditions.

4) The conversion of the synthetic polymer to its hydrochloride can be carried (within experimental error) to 100%.

Further work by the author was accordingly directed towards obtaining more detailed kinetic results to clarify the mechanisms of the main hydrochlorination reaction, and the initial fast (surface) reaction.

## 8.1. Preparation of Synthetic Latices and their Chemical Stability

Although complex emulsion polymerization methods for isoprene have been reported (50), it was found possible to prepare suitable latices with water, isoprene, ammonium persulphate (catalyst), and Vulcastab L.W. (stabilizer) as the only ingredients. Even with rather high amounts of Vulcastab L.W., a little coagulation did

occur, but the coagulum was easily removed by filtration. It had already been ascertained, of course, that the amount of stabilizer in the latex did not affect the rate of hydrochlorination.

The ingredients were sealed in pyrex ampoules which were then rotated in a thermostat for a given time. When the isoprene was sufficiently polymerized, the contents of the ampoule were filtered through glass cloth, and the latex obtained was then of fine and uniform particle size. A bluish tinge seen on the side of the ampoule was indicative of the fineness of the particles. The monomer remaining after polymerization was removed by heating the latex to 50°C under partial vacuum and blowing nitrogen or carbon dioxide over it. The latex was slightly acid (due to persulphate decomposition) and was completely stable to further acidification with hydrochloric acid, which was added to the latex, either just after its preparation, or immediately before each sample was hydrochlorinated. The concentration of hydrogen chloride in the serum of latex stored under acid conditions at room temperature never exceeded 20%, which (as discussed in Chapter 4.4.2) caused no measurable hydrochlorination over periods of months.

The latices prepared had a 15 to 20% total solids content, and the yield of polymer (excluding coagulum) was generally 30% on the monomer. The following table gives

details of the formulations and polymerization conditions.

TABLE 18

| Latex | I | II | III | V |
|---|---|---|---|---|
| Wt. of B.D.H. isoprene (gms) | 3.5 | 4.0 | 10.0 | 10.0 |
| b.p. Fraction of isoprene (°C) | 34.5-35.5 | 34.5-37.0 | 33.5-34.7 | 33.8-34.5 |
| Wt. of 20% Aqueous Soln. Vulcastab L.W. (gms) | 1.5 | 1.5 | 4.0 | 4.0 |
| Wt. of water (gms) | 1.5 | 5.0 | 15.0 | 15.0 |
| Wt. of catalyst (gms) | 0.075 | 0.085 | 0.25 | 0.25 |
| Reaction Period and Temperature | 19 hr 60°C | 4.5 hrs 57°C | 4 hr 60°C | 9.5 hr 49°C |

The initial density of the unhydrochlorinated polymer at 26.7°C ($d_o$) was determined immediately after the latex had been prepared, and also at intervals during the period of study on the particular latex. There was a slight variability in the initial density ($d_o$) of each polymer. The higher density of the polymer in latex II, for example, could be attributed to the inclusion of higher b.p. fraction of isoprene used for the polymerization.

It was observed that the density of synthetic polyispprene increased during storage, especially if the latex was unprotected from the atmosphere. The cause of this effect was traced to the ease with which the synthetic polymer was oxidized. The synthetic latices,

unlike natural rubber latex, contained no anti-oxidants, and probably oxidation was somewhat catalysed by the presence of persulphate remaining in the latex after polymerization. The consequent effect of this oxidation on the rate of hydrochlorination of synthetic polyisoprene is reported in section 8.4. The variation of initial density of unhydrochlorinated polymers had, of course, a bearing on measurements of hydrochlorination progress, since the Mole.% hydrochlorination was calculated from the change in density of the polymer during the reaction.

TABLE 19

Density Changes in Non-hydrochlorinated Synthetic Polyisoprene after Storage at Room Temperature.

| Latex | Density ($d_8$) of unhydrochlorinated polymer after preparation.(26.7°) | Density ($d_8$) of unhydrochlorinated polymer after storage.(26.7°) | Conditions of Storage. |
|---|---|---|---|
| I | 0.9043 | 0.9242 (30 days) | (a 20% HCl in serum |
| II | 0.9109 | 0.9210 (30 days) | " " " " |
| III | 0.9020 | 0.9068 (60 days) | (b no HCl in serum |
| IIIa | 0.9100 * | 0.9169 (15 days) | (a 5-10% HCl in serum. |
| V | 0.9032 | 0.9060 (60 days) | (b 20% HCl in serum. |
| Va | 0.9176* | 0.9176 (40 days) | (b 5-10% HCl in serum. |
| Vb | 0.9178* | ( 0.9250 (30 days)<br>( 0.9350 (40 days) | (b " " " |

* Vulcanized latex (See Chapter 10)
(a Latex unprotected from atmosphere
(b Latex blanketed with nitrogen

## 8.2. Maximum Conversion of Synthetic Polyisoprene to its Hydrochloride

Chlorine analyses of the final synthetic polyisoprene hydrochloride showed that 99.5% (Mole) hydrochlorination had occured (Figs. 23 and 25). D'Ianni (16) achieved a maximum conversion of 83 Mole.% when he hydrochlorinated the synthetic polymer in solution. This he ascribed to the unreactive nature of the side vinyl groups (formed by 1: 2- addition) which do not have a methyl group attached to the unsaturated carbon. He based this assumption on the knowledge that isopropyl ethylene showed no reaction with hydrogen chloride, while trimethyl ethylene reacted rapidly (51), and that he was unable to hydrochlorinate polybutadiene although polydimethyl batadiene could be reacted (52); i.e. methyl groups activate double bonds (as in rubber cyclization).

The fact that stoichiometric addition of the theoretical amount of hydrogen chloride was attained in the work for this thesis must mean that, despite the variable nature of the isoprenic groups in the synthetic polymer, they all react readily in the latex reaction with the reactive hydrogen chloride species. Further, it confirms that the incomplete hydrochlorination in other processes with various rubbers is not due to thermodynamic reversibility of the reaction (cf.Chapt.5.7).

D'Ianni et al.(15) reported that synthetic polyisoprene hydrochloride prepared from solution is amorphous. The amorphous nature of synthetic polyisoprene hydrochlorides prepared by the latex process was shown by electron diffraction experiments undertaken by Mr.J.W. Sharpe of the Natural Philosophy Department of this College. There is therefore, from these facts, a strengthening of the assumption that the premature termination of natural latex hydrochlorination is due to increasingly difficult diffusion of hydrogen chloride through the large and increasingly crystalline polymer particle (cf. 5.7)

8.3. "Ideal" Plot of Weight % Hydrochlorination against Specific Volume for Synthetic Rubber Hydrochlorides

The plot of Specific Volume (26.7°C) against Weight % Hydrochlorination (Figure 24) given by chlorine analyses of samples from synthetic latex I, is of the type explained by Gordon and Taylor (18) by the Ideal Copolymer Theory. The plot consists of two straight lines which represent respectively the rubbery and glassy copolymer states. These two lines intersect at a definite copolymer composition. The significance of such a plot may be described briefly for this thesis as follows.

The conception of ideal copolymers is analogous to that of two ideal liquids which mix without volume change, and which produce linear plots of specific

volume against Weight % composition, i.e. where the two partial specific volumes are constant. This treatment was extended to monomeric units in a copolymer, and theoretical and practical evidence was produced to show that the straight lines of such a plot as Figure 25 reflect ideal additivity of the monomer units both in the rubbery and in the glassy states.

When at a certain temperature T (at which the volume measurements are made, in this case 26.7°C), one of the pure polymers (say polyisoprene) is in the rubbery state <u>above</u> its second order trahsition temperature $T_1$, and the other pure polymer (say polyisoprene hydrochloride) is in the glassy state <u>below</u> its second order transition temperature $T_2$, then there must be a copolymer of certain composition which has its second order transition at T (here 26.7°C). This composition will be indicated by a change in the slope of the specific volume against weight % composition curve. Where the additivity of the units is ideal (linear plots), this composition is denoted by the "kink" at which the linear "rubber" and "glass" lines meet. The following theorem may be stated to summarize:

"There is a constant rubber volume ${}_iV_R$ and a constant glass volume ${}_iV_G$ at each temperature for the i th species of repeating unit in all its ideal rubbery and glassy copolymers, these two

constants being equal to the specific volume of pure polymer in these two states".

This theory is valid provided that only amorphous states are concerned or considered. One of the pure polymers may however crystallize, which would usually occur in the region of composition 80-100% of its monomeric unit, and which would lead to curvature in the specific volume plot.

The ideal nature of the plot for synthetic polyisoprene hydrochloride polymers therefore reflects the amorphous nature of the pure synthetic polyisoprene hydrochloride. Further evidence for the crystallinity of pure natural rubber hydrochloride is shown by the marked deviation downwards of its specific volume plot (Figs. 2 and 25), although the slope of its "rubbery" line is almost identical to that of the synthetic polyisoprene copolymers. Preliminary measurements by Mr. T. Carbarns in this Department, have confirmed that the "kink" at composition 82 Weight% synthetic polyisoprene hydrochloride, is, in fact, associated with a copolymer having its second order transition at 26.7°C (Fig.25).

The initial density of pure synthetic polyisoprene I at 26.7°C was 0.9043 ($d_o$), i.e. initial specific volume $V_o$=1.106. The equation for the "rubbery" line in Fig.25 is then :

$$V = 1.106 - 0.00226W \qquad \text{(Eq.5)}$$

and for the "rubbery" line of natural rubber copolymers the equation is almost identical:

$$V = 1.106 - 0.00230W \qquad \text{(Eq.6)}$$

The corresponding equation for the "glassy" line in Fig.25 is

$$V = 1.021 - 0.00124W \qquad \text{(Eq.7)}$$

where V is the specific volume of partially hydrochlorinated polyisoprene measured at 26.7°C and W is Weight% hydrochlorination.

The density of a sample of partially hydrochlorinated synthetic polyisoprene being determined at 26.7°C, V was found, and its Mole.% conversion evaluated through Eq.5 or 7, and Eqs. 4 and2 (p.11).

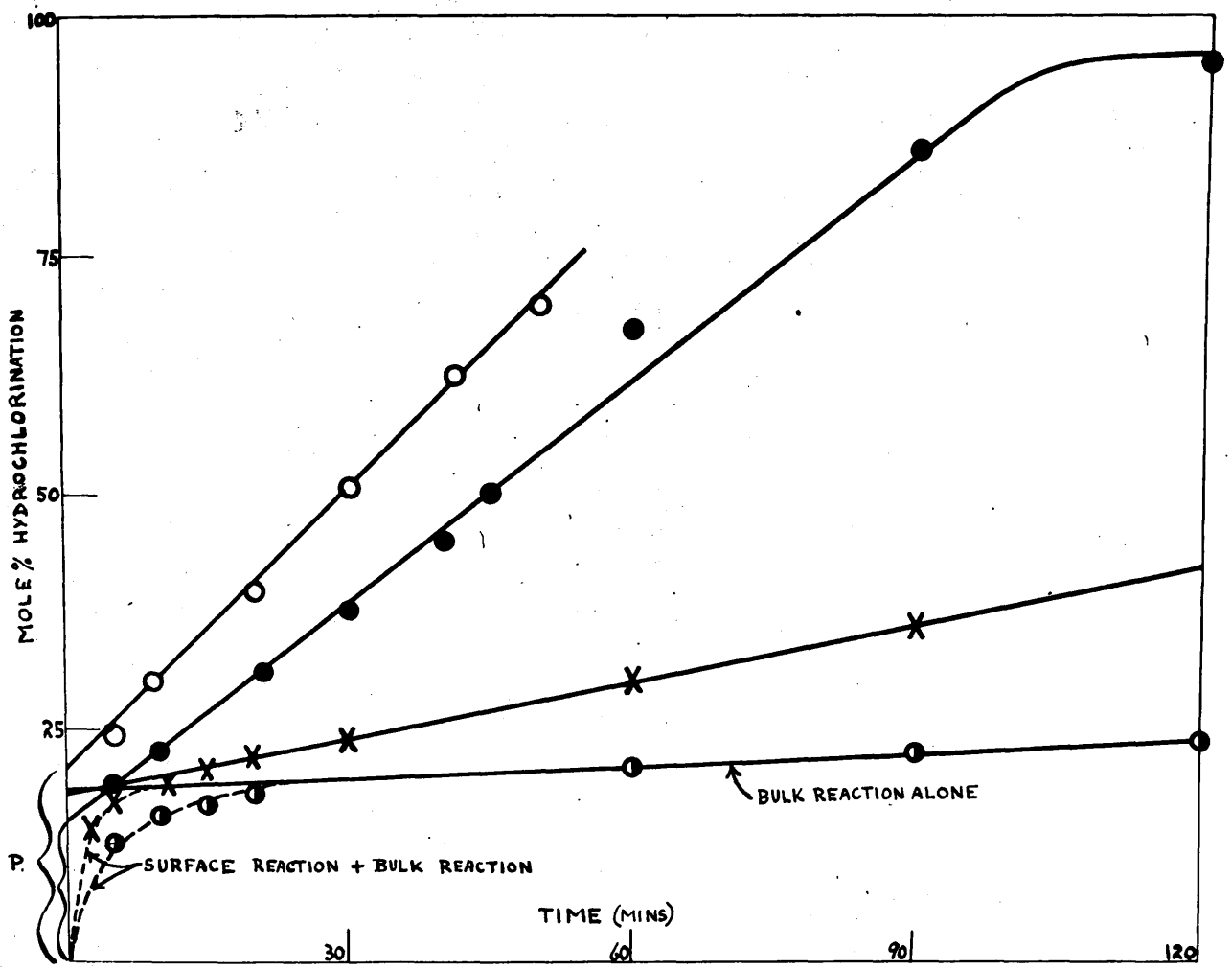
Where the specific volume of the starting polymer ($V_o=1/d_o$) was higher or lower than 1.106, Eq.5 was adjusted accordingly, and a similar parallel displacement was also made for the "glassy" line. This procedure was in accordance with the Ideal Copolymer Theory which assumes that the conversion of each isoprene unit to its hydrochloride causes a constant volume change irrespective of the initial $V_o$.

For each latex, the value of $V_o$ which prevailed during kinetic experiments on it, is tabulated along with the relevant kinetic results in the tables in the Appendix (22-25, 28-37).

## 8.4. Identification of the Initial Fast Rate Abnormality as a Surface Reaction

When the relevant straight line portions (representing the main rate $k_2$) of the kinetic curves for the hydrochlorination of synthetic latices I andII and natural latex are extrapolated back to the composition axis (Fig.23), it is revealed that different percentages, P,of the total polymer are involved in the initial "jump", (measured from the runs at 26.7°C). The percentages are 2.0% for natural latex, 6.25 for synthetic latex I, and 20.0% for synthetic latex II. This fast reaction must be due to the presence of corresponding percentages of isoprene units which are either lying at a site more favoured for reaction, or which have a chemically more reactive structure.

The former concept was supported when electron microscope measurements were undertaken by Mr.J.W. Sharpe. These revealed that the particle size of latex I was about three times that of latex II, and so focussed the initial fast rate as a surface effect involving a percentage P of units lying at or near the particle surface. Hydrochlorination kinetics and electron microscope measurements,next carried out on synthetic latices LII and V,further established the correlation between P and the latex particle size (Fig.26 and Table 20). The




COMPARISON OF SYNTHETIC LATICES III AND V, AND PROGRESSIVE ISOLATION OF SURFACE LOCUS

FIG. 26

- O SYNTHETIC LATEX V HYDROCHLORINATED AT 26·7°C, 2 ATM. HCl. } THESE TWO PLOTS ILLUSTRATE MAXIMUM DIVERGENCE IN SLOPE
- ● SYNTHETIC LATEX III HYDROCHLORINATED AT 26·7°C, 2 ATM. HCl. }
- X SYNTHETIC LATEX III HYDROCHLORINATED AT 69·5°C, 1·95 ATM. HCl.
- ◑ SYNTHETIC LATEX III HYDROCHLORINATED AT 69·5°C, 0·91 ATM. HCl.

percentage P of "fast"units increased with each reduction in particle size (diameter D) as is illustrated in Table 20

Table 20

| P% (26.7°C,2 Atm. HCl) | D (unshadowed) Ave. Particle Diameter (Å) | t (Shell thickness) (Å) | Latex |
|---|---|---|---|
| 2.0 | 4500(Ref.53) | 15 | Natural |
| 6.25 | 1175 | 12.5 | Synth. I |
| 15.0 | 670 | 15 | " III |
| 20.0 | 467 | 17 | " II |
| 21.0 | 460 | 17.4 | " V |

It is therefore postulated that the extent of the initial fast reaction, at a given temperature, is governed by only the percentage P of the isoprene units lying within an outer shell of thickness $\underline{t}$ on the surface of the particles. Or, in other words, for any latex, the thickness $\underline{t}$ of the outer shell in the particles should be constant, at a given temperature, and should be comprised of the relevant percentage P by volume of the average particle (spherical, diameter D) of the latex in question.

Table 20 above records the P, D, and $\underline{t}$ for each of the latices studied, and the constant value of $\underline{t} = 15 \pm 2.5$ Å confirms that the surface reaction is indeed restricted to the outer three or four layers of polymer chains in the particle. This shows, indirectly, that the

subsequent reaction(of zero-order rate $k_1$ and/or $k_2$) occurs at the other possible locus, namely, inside the bulk of the polymer particles.

Values of t are calculated from the equation:-

$$t = \frac{D}{2}\left(1 - \left(\frac{100 - P}{100}\right)^{1/3}\right) \qquad \text{(Eq.8)}$$

The fact that the surface reactive units lie within 15 Å of the surface, means that for particles,of D greater than 500 Å, the intercept P is, in fact, accurately proportional to the specific surface of the particles.

The narrow size range of the synthetic latex particles, allows sufficiently accurate values of diameter D to be obtained by averaging a few particles chosen at random on the electron micrographs. Natural Hevea latex particles are far from uniform, and the value of D = 4500 Å reported by van den Tempel (53) is taken for Table 20. A full-size analysis does not seem necessary, considering the limited relative accuracy of the intercept of natural latex (P= 2.0± 0.5). The total range of average particle diameter is seen to be 10-fold.

Electron microscope measurements also showed that the particle size remained essentially the same, unchanged, during the reaction, thus confirming that no coagulation or dissolution of the particles occurs.

(Volume changes caused by the actual addition of hydrogen chloride to the polymer could be calculated from density data, but this effected a change of only a few per cent on the particle diameter).

The isolation and subsequent hydrochlorination of fine and coarse fractions of Hevea latex, suggested by Mr.C.Moss of the Dunlop Rubber Co., (cf. Chapter 5.5), constituted the final proof of the surface reaction. Here, as illustrated in Fig.21, the intercept P is indeed increased and decreased respectively for the fine and coarse fractions. Electron microscope measurements showed that the average size of particle in the fine fraction was one-third of that in the whole latex; the intercept for the fine fraction is three times that of the whole latex.

Hydrochlorination kinetics can therefore furnish a method of measuring the surface average particle diameters of polyisoprene latices through measurements of P and Eq.8.

The rate of surface hydrochlorination at 26.7°C, 2 Atm. HCl occurs immeasurably fast, although extrapolation gives exact measurement of its extent, Figs. 23 and 26. The reaction rate is progressively reduced on going to 69.5°C, 1.95 Atm. HCl and 0.91 Atm. HCl, where the surface reaction becomes apparent as the initial rounded portion of the rate

curve (synthetic latex III, Fig. 26). These initial rounded portions represent the combined effect of the surface locus rate plus the main bulk locus rate. Even at 69.5°C, 0.91 Atm. HCl, the initial curved portion of the kinetic plot merges into the line of finite slope representing the main rate $k_2$, but experiments described in Chapter 10, show that the surface locus hydrochlorination can be isolated if the hydrogen chloride pressure is so reduced as to eliminate the bulk reaction.

The mechanisms of hydrochlorination at these two loci are different and will be discussed in the next two chapters. It need only be stated here, that two pieces of kinetic evidence regarding the surface reaction indicated it as being controlled by a diffusion process. Firstly, at constant HCl pressure, the thickness $t$ (i.e. P) increases with temperature. Secondly, the surface reaction falls off rapidly with reaction progress and becomes negligible once the first three or four layers have been hydrochlorinated.

## 8.5. Comparison of the Main Rates of Hydrochlorination ($k_2$) of Synthetic Polyisoprene and Natural Rubber Latices

Figs. 23, 24 and 26 show that in the hydrochlorination of synthetic latices, the retardation effect, which leads to a slow linear rate $k_1$ before the full rate $k_2$ is suddenly attained, is entirely missing.

This confirms that the retardation effect is not an essential part of the mechanism (cf. Chapter 5.5.).

Further it was found that the full (unretarded) zero-order rates of hydrochlorination ($k_2$) of natural rubber latex are reproduced almost identically when the synthetic substrate is reacted under similar experimental conditions. This is demonstrated by the parallel straight line portions of the kinetic curves in Fig.23, and is also shown in the table below which records the main bulk reaction rates $k_2$ for all the latices studied under the various conditions of temperature and pressure.

TABLE 21

| Latex | Temp. °C | Total Pressure. Atm. HCl + $H_2O$ | Pressure Atm. HCl | Rate Mole.%/hr |
|---|---|---|---|---|
| Hevea | 0 | 1 | 1 | 12.5 |
| Hevea | 0 | 2 | 2 | 181.0 |
| Hevea | 26.7 | 1 | 1 | 5.2 |
| Synthetic II | 26.7 | 1 | 1 | 5.6 |
| Hevea | 26.7 | 2 | 2 | 47.5 |
| Synthetic I | 26.7 | 2 | 2 | 51.0 |
| Synthetic II | 26.7 | 2 | 2 | 51.0 |
| Synthetic III | 26.7 | 2 | 2 | 47.0 |
| Synthetic V | 26.7 | 2 | 2 | 57.5 |
| Hevea | 69.5 | 1 | * 0.91 | 2.5 |
| Synthetic III | 69.5 | 1 | * 0.91 | 3.0 |
| Hevea | 69.5 | 2 | * 1.95 | 15.5 |
| Hevea (Fine fraction) | 69.5 | 2 | * 1.95 | 12.0 |
| Synthetic III | 69.5 | 2 | * 1.95 | 12.0 |

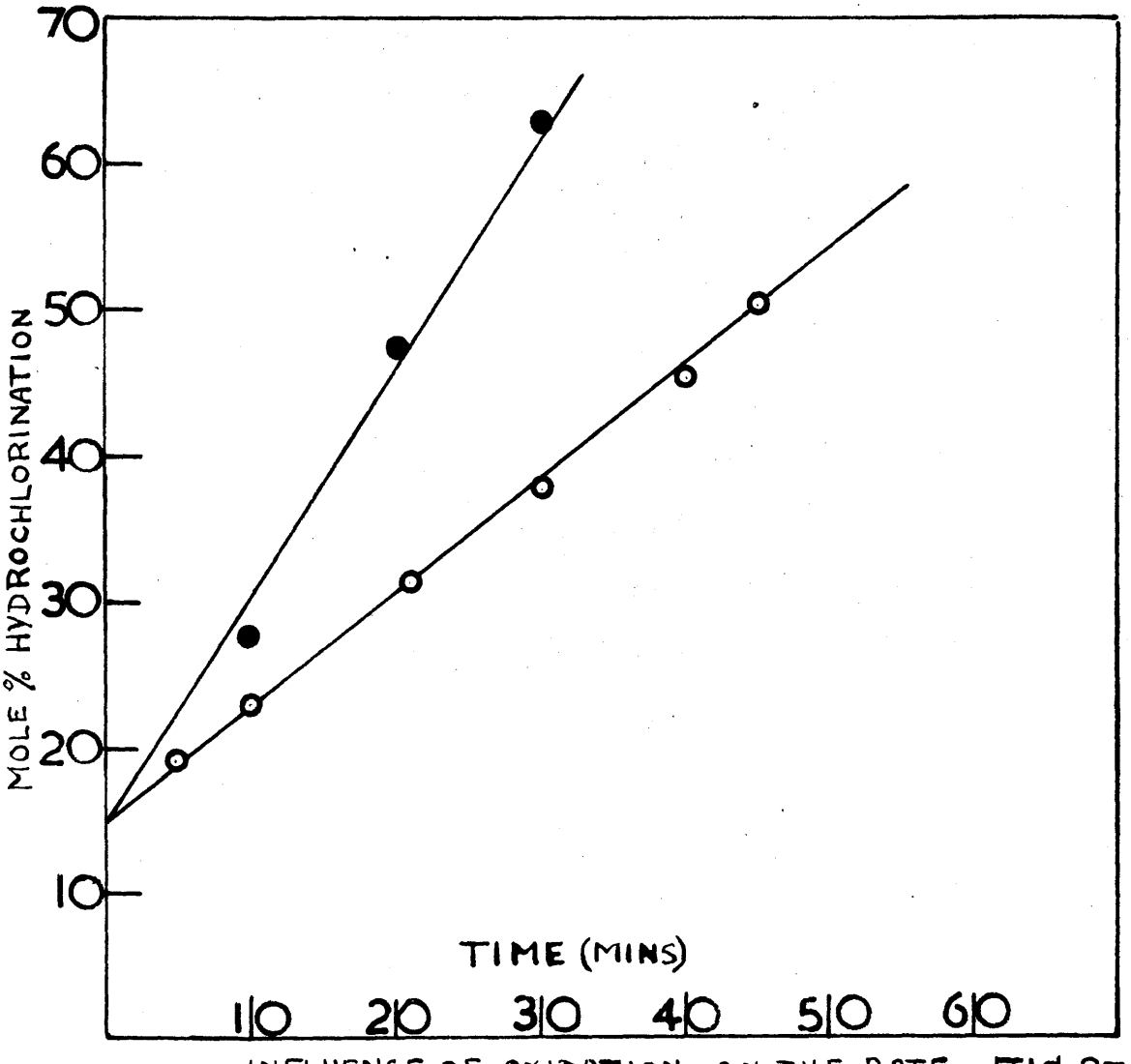
* Computed by interpolation in International Critical Tables through subtraction of the equilibrium water vapour pressure.

The reproduction of similar reaction rates for the two substrates led to the reaction mechanism proposed in the next chapter.

It can be seen from Table 21, that a 70-fold range in the main zero-order rate $k_2$ was achieved through the adjustments of temperature and pressure. It can also be noted that variations do exist in the bulk rate of hydrochlorination under a given set of experimental conditions. These variations do not exceed 25 %, which, although relatively small considering the 70-fold range covered, require some discussion, because the theory of rate control by a purely inorganic step does not envisage such variations. Fig.26 shows that the difference in rate (slope) of hydrochlorination of synthetic latices III and V at 26.7°C, 2 Atm. HCl, is quite outside experimental error, but that both are zero-order plots, i.e. linear.

Crampsey observed that after latices I and II had been stored for about 4 weeks (20% HCl in serum), the kinetic samples then taken, were further hydrochlorinated (i.e. denser) than expected (full circles and triangles in Fig.23). Estimations on the original unhydrochlorinated polyisoprene revealed a density increase, but without a corresponding increase in chlorine content.

It was later shown by the author that




INFLUENCE OF OXIDATION ON THE RATE OF HYDROCHLORINATION OF SYNTHETIC LATEX

FIG. 27

O···· FRESH SYNTHETIC LATEX III AT 26·7°C, 2 ATM. HCl.

●···· SYNTHETIC LATEX III OXIDIZED BY MAKING AMMONIACAL AND LEAVING OPEN TO ATMOSPHERE FOR 4 DAYS BEFORE REACTING AT 26·7, 2 ATM. HCl.

this density increase was due only to oxidation of the polymer, and the effect of this on the rate of hydrochlorination was examined as follows. Latex III, which had been stored without acidification, was made alkaline with 0.06% ammonia, and was allowed to stand exposed to the atmosphere for 4 days. After this period, the density of the non-hydrochlorinated synthetic polyisoprene had increased from 0.9020 to 0.9115. The oxidized polymer was then hydrochlorinated and it was found that the main reaction rate $k_2$ was greatly increased (Fig.27) . The zero-order nature of the plot prevailed however, and the surface reaction was unaffected.

The small variations in the bulk rates of synthetic polyisoprene may therefore be ascribed to the effect of slight oxidation of the polymers during their preparation (no correlation between density and amount of oxidation has been noted so far).

According to the theory of reaction mechanism discussed in the next chapter, the increased bulk rate reflects a faster formation of the reactive hydrogen chloride species ($H^+$,$Cl^-$) in the oxygenated polymer particles. This is reasonable as the introduction of oxygenated functions into the rubber, renders it more similar to the aqueous medium, where reactive species are formed with great speed. Also it is

in line with the mechanism proposed, that the bulk rate remained linear and the surface rate unaffected by the oxidation effect, and the minor variations in the main rate constituted no serious objection to the theory.

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CHAPTER 9

## Rate Controlling Mechanism of Hydrochlorination of Synthetic and Natural Polyisoprene Latices.

It has been seen that, despite the differences in the detailed structure of the polymer, nearly identical zero-order rate constants apply to both substrates for the bulk hydrochlorination, which covers 60-70% of the reaction.

The zero-order kinetic law may be explained *a priori* by either of two contrasting hypotheses.

1) The rate-determining step involves the polymer, but the disappearance of the polymer units caused by hydrochlorination leaves the rate unaffected for special reasons of compensation, such as might arise in a chain reaction mechanism.

2) The rate-controlling step involves only species derived from hydrogen chloride, and possibly water, whose concentrations are maintained constant in the surrounding aqueous phase during each experimental run.

Since stereochemical considerations lead to the postulate of a chain reaction for the hydrochlorination of Hevea latex (Chapter 6), it is necessary to discuss 1) in some detail. The discussion will show that this hypothesis is extremely unlikely, since any zero-order rate obtained must be sensitive to the number or kinetic length of the chains involved, which in turn must be

sensitive to the detailed structure of the polymer and could hardly survive unchanged a change of substrate from rubber to synthetic polyisoprene. Zero-order kinetic laws can arise in the following two basic types of chain mechanisms.

1a) Life-time of Reaction Chain Comparable with Total Reaction Time. In the kinetic curves, a long linear portion followed by a rounded portion leading to asymptotic decay has been observed. Jellinek (54) has given a relevant plot in connection with certain degradation mechanisms of vinyl polymers, and such a plot could be fitted to the results for the main hydrochlorination of rubber and synthetic polyisoprene. The straight-line portion must then be the result of a constant number of reaction chains, started simultaneously at the beginning of the reaction, and propagated with constant average rate. Initiation must then occur at chemically privileged units of the polymer chain, and the propagation must pass along the chain. To ensure a constant length of polymer between them (i.e. a constant kinetic chain length), the privileged units must be very evenly spaced along the polymer. The privileged units cannot be merely end units, since the polymer chains in rubber are far from constant in length. The kinetic chain length must be about 30 units or more. If these conditions do not apply, the linear portion of the kinetic curves will be shorter than was observed. The

rounded portion at the final stages of the reaction is, of course, due to the fact that the chains, though initiated simultaneously and of even chain length, will not die simultaneously. Their life-time would be governed by a Poisson type distribution, because propagation is subject to the hazard of random encounters.

The theory that a small number of evenly spaced, chemically reactive, initiating groups might be present in natural rubber was previously entertained, but the same number and spacing of such groups cannot possibly be characteristic of the synthetic polyisoprene, and so mechanism 1a) must be abandoned.

1b) Life-time of Reaction Chain Small Compared with Total Reaction Time. In this hypothesis the following equation would apply:

Overall Rate = Initiation Rate x Kinetic Chain Length

By the constancy of the two factors on the right hand side (as in certain photochemical experiments), or by their reciprocal variation, a linear rate law may be achieved. However, both factors again depend critically on the detailed structure of the polymer units, so that it is again impossible to understand how the same constant rate could be achieved for both the natural and synthetic substrates. It is thus evident that the presence of a chain reaction magnifies the sensitivity of the most

of the most stringent test for non-participation of the substrate in the rate-controlling step, namely, an actual change of substrate. It has already been mentioned that Ingold et al.(48) explained the zero-order nitration of organic substrates as being controlled by the rate of reaction $O_2N.OH \longrightarrow O_2N^+ + OH^-$.

The rejection of schemes 1a) and 1b) demands, in accordance with hypothesis 2) above, the search for a rate-determining step which involves only the hydrochloric acid (and possibly water) for the hydrochlorination of the polyisoprenes.

Nature of the Rate-Controlling Step. The rate of this step will follow the fundamental Brønsted equation:

$$\text{Rate} = k a_1^m a_2^n \ldots / f_T \qquad \text{(Eq.9)}$$

where the a's are the activities of colliding species, and $f_T$ is the activity coefficient of the transition state. The main hydrochlorination takes place in the hydrocarbon phase and probably between ions as will be shown. It therefore falls into a class of reactions for which there is little knowledge to draw on. Nevertheless, a concrete suggestion as to the nature of the rate-controlling step emerges from the temperature and concentration effects measured.

Since the partial pressures of hydrogen chloride and water (almost negligible) are constant for

each kinetic run, the activities of all species which are in equilibrium with these vapours will likewise remain constant. The rate-controlling step must produce a highly reactive species (cf. $NO_2^+$ for nitration) from certain precursors (cf. $O_2N.OH$ for nitration). The highly reactive species will be immediately taken up by the rubber substrate as soon as they are formed. The precursors are here in diffusive equilibrium with the aqueous and hence with the vapour phase, as otherwise the a's in equation 9 would vary, and zero-order rate plots would not be obtained over wide ranges of temperature and acid pressure. If the precursors can be maintained in diffusive equilibrium across the rubber particle surface, the same must be true of neutral covalent hydrogen chloride molecules, which are the stable dissolved species in hydrocarbon media. This is confirmed by the finding of Wynne Jones (55) that the small amount of hydrogen chloride dissolved in benzene (saturated with water) at 25°C follows Henry's law of pressure against mole fraction. (The slope of the line, incidentally, lies well below 50% of that for Raoult's law, thus showing that the solution is not an ideal one).

If hydrogen chloride molecules are in diffusive equilibrium with the aqueous phase, they cannot constitute the reactive species formed in the rate-determining step, whose equilibrium must be completely upset by the fast reaction with rubber. The rate of

hydrochlorination (grams of HCl per cc. of latex per second) is proportional to the rubber concentration. But if the reactive species were in diffusive equilibrium, the rate of hydrochlorination would be independent of the rubber concentration (i.e. the rubber would behave like a dissolved species in the zero-order reaction, not like a separate phase).

Another important conclusion may be derived from the constancy of the rate between about 20 and 80% hydrochlorination. According to equation 9, $f_T$ as well as the a's must be constant, and this despite the considerable change in the reaction medium (especially the dielectric constant) which occurs as rubber is progressively converted to rubber hydrochloride. This constancy of $f_T$ must mean that there is no net charge on the transition state which converts the precursors into the reactive species (56).

The unknown true activation energy of polyisoprene hydrochlorination may be expected to be considerable (say, greater than 15 k cals), since a H-Cl bond must be broken and a C=C converted to a C-C bond. The apparent activation energy, at constant activity (pressure) of hydrogen chloride, is an appreciably negative quantity, -5.3 kcals. on an average for natural rubber at 26.7°C, 1 Atm. HCl. Such a decrease in rate with rising

temperature, is generally to be explained as due to a pre-equilibrium, producing reaction precursors exothermally, and thus, by le Chatelier's principle, reducing their activities in equation 9 with rising temperature. It is unlikely that the pre-equilibrium, with an exothermic forward reaction, which is concerned here is merely the dissolution of hydrogen chloride gas in the polymer particles, as the heat of dissolution can hardly be large enough to depress the apparent activation energy so markedly.

If hydrogen chloride were an ideal solute in rubber, this heat of solution could be equated to its heat of condensation (into pure liquid HCl), namely, about 3.5 kcals. Even if the true value were twice as great, and two separate hydrogen chloride molecules were required as precursors, the resulting depression of the activation energy, 2 x 2 x 3.5 = 14kcals., still falls well below the expected range.

It seems likely then, that the effect of a chemical equilibrium is superimposed on the dissolution equilibrium, thus subtracting a further substantial heat of reaction from the heat of formation of the actual precursors in the polymer phase, and thus adding it to the activation energy. This suggests that the precursors are ionic, because un-ionized derivatives of hydrogen chloride would hardly be substantially exothermic. The

heat liberated in the formation of ions may be called a "heat of solvation", but little is known about the nature of ion solvation in wet hydrocarbon media.

These various strands of evidence combine to suggest that the rate-controlling step is the formation of an uncharged, but not covalent, form of hydrogen chloride from ionic precursors. This means that a neutralization step creates an "ion pair" as the reactive species which combines with the polyisoprene.

Disregarding solvation, we may write this as

$$H^+ + Cl^- \longrightarrow (H^+,Cl^-) \qquad \text{(Eq.10)}$$

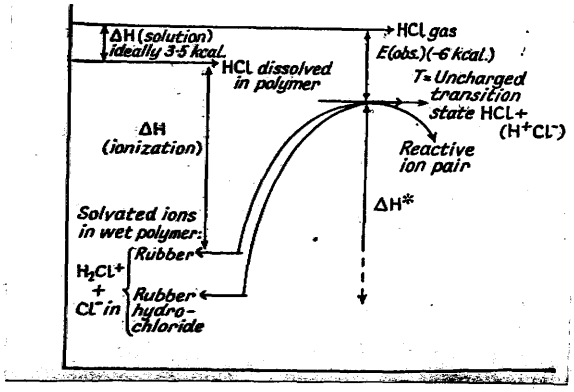
In water, $H^+$ is known to be solvated as $H_3O^+$, but the high dependence of the isothermal rate of hydrochlorination of rubbers on hydrogen chloride pressure favours the assumption that $H_2Cl^+$ is concerned as the positively charged precursor in the rubber phase. (The concentration of $H_2Cl^+$ will probably be governed by an acidity function $H_o$). Reaction 10 may therefore prove to be more correctly written:

$$H_2Cl^+ + Cl^- \longrightarrow (H^+,Cl^-) + H\text{-}Cl \qquad \text{(Eq.11)}$$

The right hand side of equation 11, as regards the formation of a reactive ion pair, is more certainly indicated by the present kinetic evidence than the precise nature of the precursors on the left.

Fig. 28 sketches qualitatively the possible energy levels for the early steps in the hydrochlorination reaction, up to the reactive ion pair (which converts an isoprene unit into its hydrochloride very quickly). This sketch brings out the fact that the observed activation energy (E) is negative and constant, leading to a constant rate independent of reaction progress at each temperature, while the true activation energy $\Delta H^*$ is positive and may vary with the reaction progress. Although the energy level of the ionic

FIG. 28 *Possible energy levels of precursors in hydrochlorination.*




precursors should drop as the dielectric constant of the polymer increases because of the hydrochlorination progress, the level of the transition state T, which bears no net charge, remains unaffected. Any understanding of this complicated reaction is due to this. Fig 28 implies that the formation of the rubber hydrochloride from gaseous hydrogen chloride and rubber must be exothermic to at least the extent of the observed

energy of activation (-5.3 kcals.), since the energy level of rubber hydrochloride must lie below that of the transition state T. According to reaction 11, this state will not differ greatly from two hydrogen chloride molecules in collision, which agrees well with its observed energy level 5.3 kcals below the gas, since this represents closely the level of two hydrogen chloride molecules regarded as an ideal solute (approx. 7 kcals. below the gas).

Since the main barrier in the overall addition of gaseous hydrogen chloride to rubber must be the breaking of the H-Cl bond, and since ion pairs are familiar species in media of low dielectric constant (57) (58) the reactive species proposed may be accepted with considerable confidence: it presents the polyisoprene with the elements of hydrogen chloride, but with the covalency broken.

The reaction of double bonds with ion pairs in ionic polymerizations is becoming increasingly apparent, and studies on polymerization of styrene especially have given evidence for ion pair mechanisms (59). Overberger and Endres (60) have shown the possibility of assigning a nucleophilic factor for attack of ion pair on aromatic-type nuclei.

It is interesting to note that Harned and Seltz (29) demonstrated the effect of hydrogen chloride activity in kinetics in their study of the conversion of acetyl chloro-amino-benzene to p-chloro-acetanilide . In the concentration range up to 0.2M acetyl chloro-amino-benzene, the apparent first-order rate constants were found to be accurately proportional at each temperature to the activity products $a_{H^+} a_{Cl^-}$ (up to molar HCl). The reaction steps were proposed as:

$$C_6H_5NClCOCH_3 + H^+ + Cl^- \longrightarrow C_6H_5NHCOCH_3 + Cl_2$$

$$C_6H_5NHCOCH_3 + Cl_2 \longrightarrow ClC_6H_4NHCOCH_3 + H^+ + Cl^-$$

The rate constants vary, and therefore the activity product varies with hydrogen chloride concentration in a parallel manner between 17 and 35°C. Since triple collisions are rare, an ion pair seems more likely to be presented, as a more reactive species, to the acetyl chloro-amino-benzene. Measurements of activity products in the HCl concentration required for polyisoprene hydrochlorination could possibly reveal a similar correlation with rate measurements.

The chain reaction mechanism proposed for latex hydrochlorination of natural rubber (cf. Chapter 6) requires that the hydrogen chloride must react in a form bearing no net charge with the chain-carrying rubber units,

in order to leave their charge-type unchanged. The deduction of an ion pair as the reactive species, based in particular on the constancy of $f_T$ with reaction progress, is a gratifying confirmation of this. However, according to the nature of the rate control, revealed as a purely inorganic step, no other contact with the chain reaction theory has emerged from the kinetic data. Since the rate-determining step (Eq.11) is merely a preliminary to the attack on the polyisoprene, the kinetics are equally compatible with reaction chains passing along the polymer molecules, and with non-chain (random) mechanisms. If the specific chain mechanism for natural rubber is correct, very different reaction steps are likely to succeed the rate-controlling step in rubber and in synthetic polyisoprene because of the structural differences in the two substrates. All succeeding steps must, in the light of the observed kinetics, occur rapidly with respect to the life-time of the reactive ion pair.

The zero-order main rate of hydrochlorination has been demonstrated to occur within the bulk of the polymer particle, while the fast initial high-order hydrochlorination rate is due to a reaction at the particle surface. The effect of diffusion rates of hydrogen chloride species does not enter into the rate-control of the bulk hydrochlorination. The reactive ion pair is snapped up by the polymer as soon as it has

formed, presumably without having to travel far in search of an unsaturated unit, at least until the final stages of the reaction. In any event, fundamental work by Grün (61) on diffusion in rubber, has shown that the controlling factor is the size of the diffusing species, so that entities of the size of HCl would diffuse through rubber at rates of the same order as through water (approx. $10^{-2}$ times as fast).

In this connection, it is of interest to note some measurements of HCl diffusion into wool fibres. Hudson (62) has reported diffusion coefficients of $3 \times 10^{-5}$ $cm.^2.sec^{-1}$ for HCl in aqueous solution, and $8 \times 10^{-9}$ $cm.^2.sec^{-1}$ for HCl in wool at 18°C. Peters and Lister (63) quoted a diffusion coefficient of $1.2 \times 10^{-10} cm^2.sec^{-1}$ for HCl in wool at 40°C, and reported that fibres of mean radius 13μ were saturated in 30 minutes at 40°C. Since the rate of diffusion in rubber may be taken to be of the order $10^3$ times that in wool (rate of saturation inversely proportional to radius$^2$, and from Grün and Hudson's data), then a rubber particle (0.5μ, or less for synthetic latex) becomes saturated in less than a thousandth of a second. In the bulk hydrochlorination reaction therefore, the polymer particles are sufficiently small to allow diffusive equilibrium of ionic precursors to be maintained. The concentration of these in the rubber is dependent on HCl pressure but is generally extremely small because of poor solvent properties of the hydrocarbon polymer.

/properties of the hydrocarbon polymer.

The mechanism of rate control for the surface hydrochlorination, on the other hand, is one of diffusion, as will be explained in the next chapter. In this case however, the reaction rate is controlled by the life-time of the reactive species in the hydrocarbon medium before it is itself decomposed.

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# CHAPTER 10

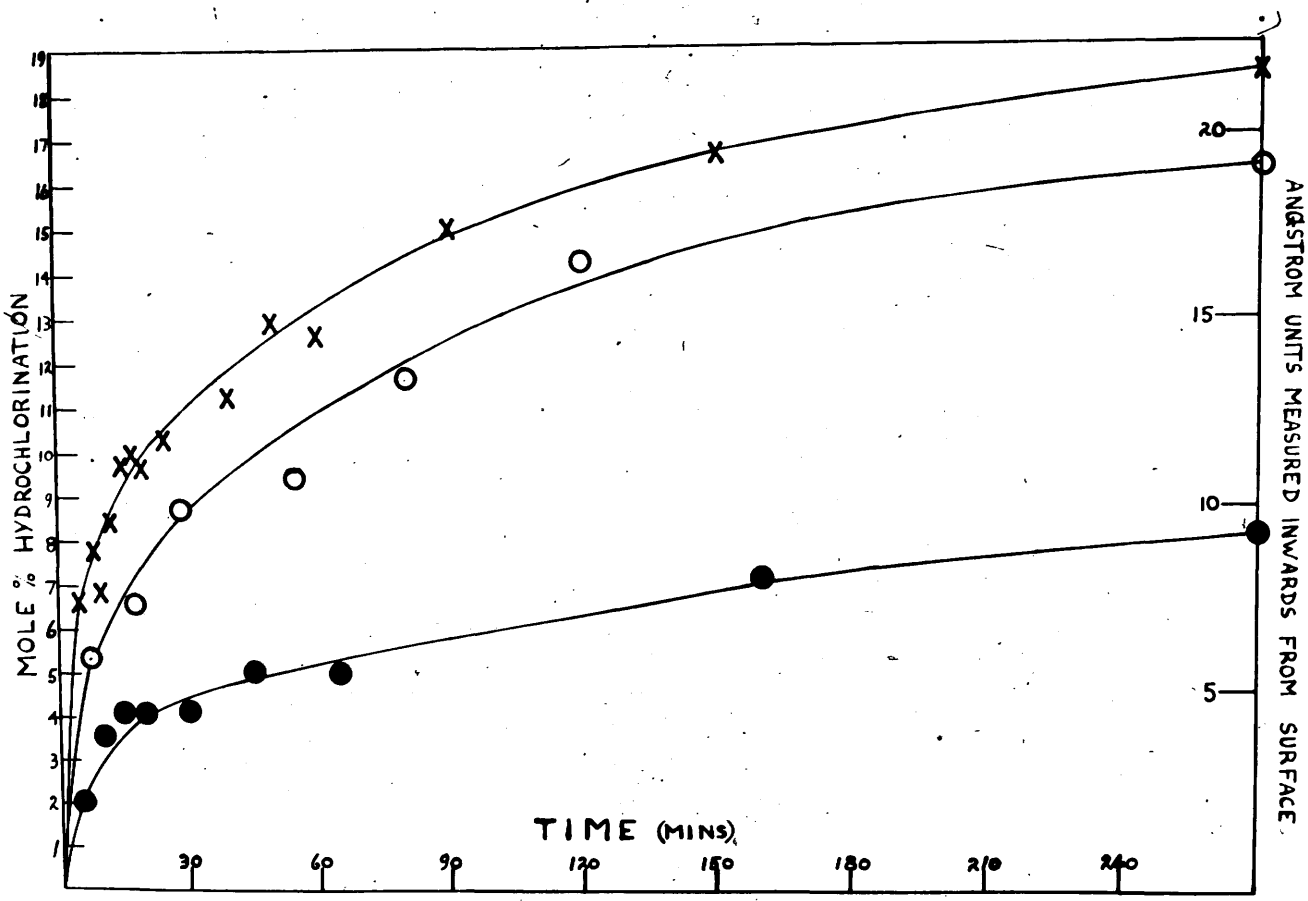
## Kinetics of the Isolated Surface Locus Reaction in Unvulcanized and Vulcanized Latices: Diffusion Mechanism

### 10.1. Results and Conclusions from the Kinetic Isolation of Surface Hydrochlorination in Synthetic Latices.

Fig. 26 shows successive stages in the kinetic isolation of the surface effect in synthetic latices, brought about by slowing down the total hydrochlorination rate. It was found that by carrying out the reaction at HCl pressures far below atmospheric (previously taken by van Veersen (17) as the lower limit for his reaction), the bulk reaction, taking place within the polymer particles, could be effectively eliminated(64). At 26.7°C in the region of 0.33 Atm HCl where the most useful measurements have been made, the bulk rate is indeed negligible, and, even at 0.08 Atm HCl, the units that react by the surface locus mechanism do so at appreciable speed.

The apparatus described in Chapter 4.4.5. was employed for the hydrochlorination experiments at reduced pressure.

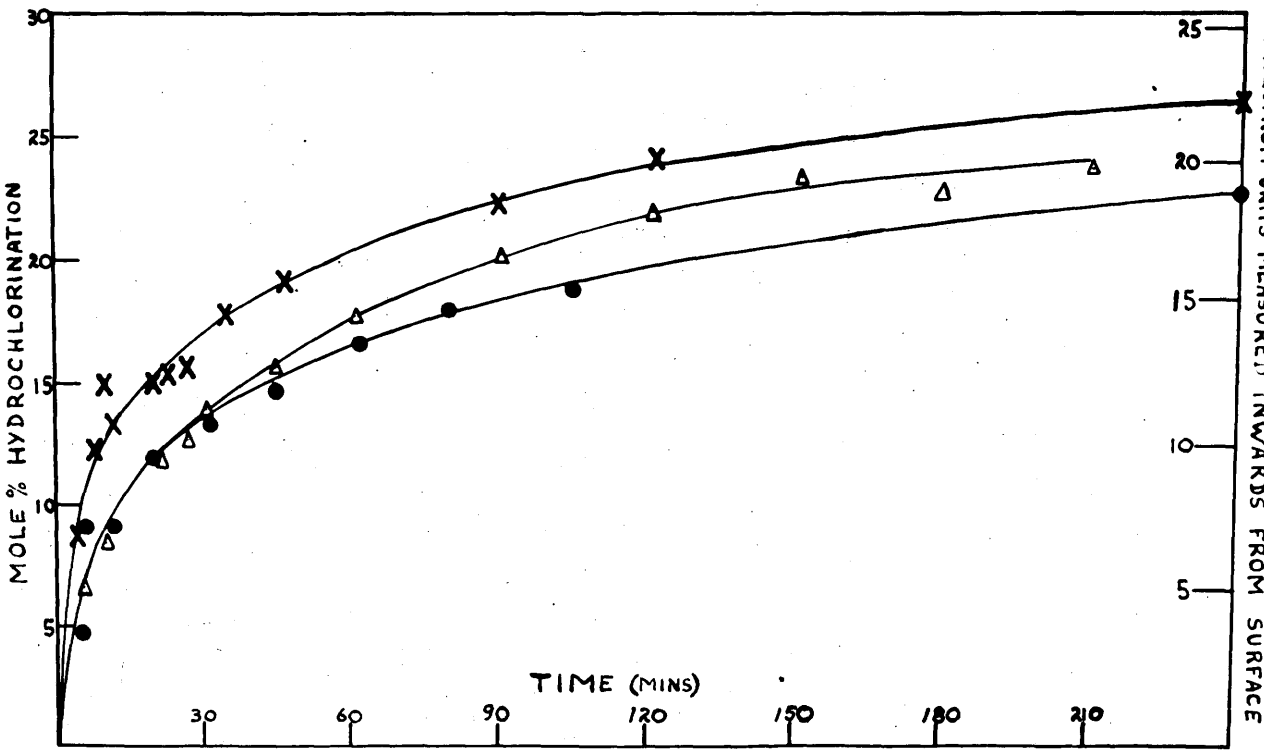
Figs. 29 and 30 illustrate the kinetic curves for the isolated surface effect. The rate of surface hydrochlorination at constant temperature is decreased as the pressure is lowered. These curves serve as a warning that the measurement of chemical equilibrium




SURFACE LOCUS RATE CURVES FOR HYDROCHLORINATION AT 26·7°C

FIG. 29

X UNVULCANIZED SYNTHETIC LATEX III AT 0·33 ATM. HCl.
● UNVULCANIZED SYNTHETIC LATEX III AT 0·08 ATM. HCl.
○ VULCANIZED SYNTHETIC LATEX III AT 0·33 ATM. HCl.




SURFACE LOCUS HYDROCHLORINATION RATE CURVES. FIG. 30

X ..... SYNTHETIC LATEX V AT 26·7°C 0·33 ATM. HCl.

● ..... SYNTHETIC LATEX V AT 26·7°C 0·22 ATM. HCl.

Δ ..... SYNTHETIC LATEX V AT 69·5°C 0·22 ATM. HCl. (APPROX. FROM INT. CRIT. TABLES)

properties such as unsaturation by a latex technique (30) must be considered by cautious reference to kinetics and reaction loci. For example, it must not be inferred from the run at 0.33 Atm HCl (Fig 29) that only 19-20% of the units in synthetic latex III were unsaturated, but rather that this was the percentage of units which lay within range of the surface locus mechanism. The scale on the right hand side of the curves in Figs. 29 and 30 converts % reaction to range of reaction from particle surface (in Å), to which % reaction is equivalent. It is evident that the units within the first 4-5 Å (i.e. surface layer) react quickly.

The general significance of the curves in Figs. 29 and 30, is that a certain proportion of the polymer units lie in a privileged position near to the aqueous acid phase to be reacted by a mechanism not available to units further inwards in the bulk of the particles. As the distance of a unit from the interphase increases, its chance of reaction by this mechanism decreases sharply, and the originally steep rate curve quickly levels off, i.e. the reaction is of high order. The conventional equation,

$$\int dx/(a-x)^n = (n-1)^{-1}\{ (a-x_t)^{-n+1} - a^{-n+1} \} = kt \quad \text{(Eq.12)}$$

produces a linear plot for synthetic latex III (26.7°C, 0.33 Atm. HCl) when the reaction order is taken as 26, i.e.

the rate falls off as the 26th power of the per-centage of units in the particles which remain unreacted.

The kinetic evidence suggests that the falling off of the surface reaction rate is governed by a diffusion rate process. The bulk reaction has been postulated as controlled by the relatively slow rate of formation of ion pairs in the polymer. But in the aqueous phase the reactive hydrogen chloride species might well be formed very much more rapidly and be in plentiful supply. They may then attack the surface layers very quickly under conditions where the rate in the bulk of the particle is negligible.

Two different diffusion processes then come under consideration :

a) A constant concentration of the active HCl species exists in the aqueous phase, and polymer chains diffuse outwards to the interphase where the unsaturated bonds are instantly reacted.

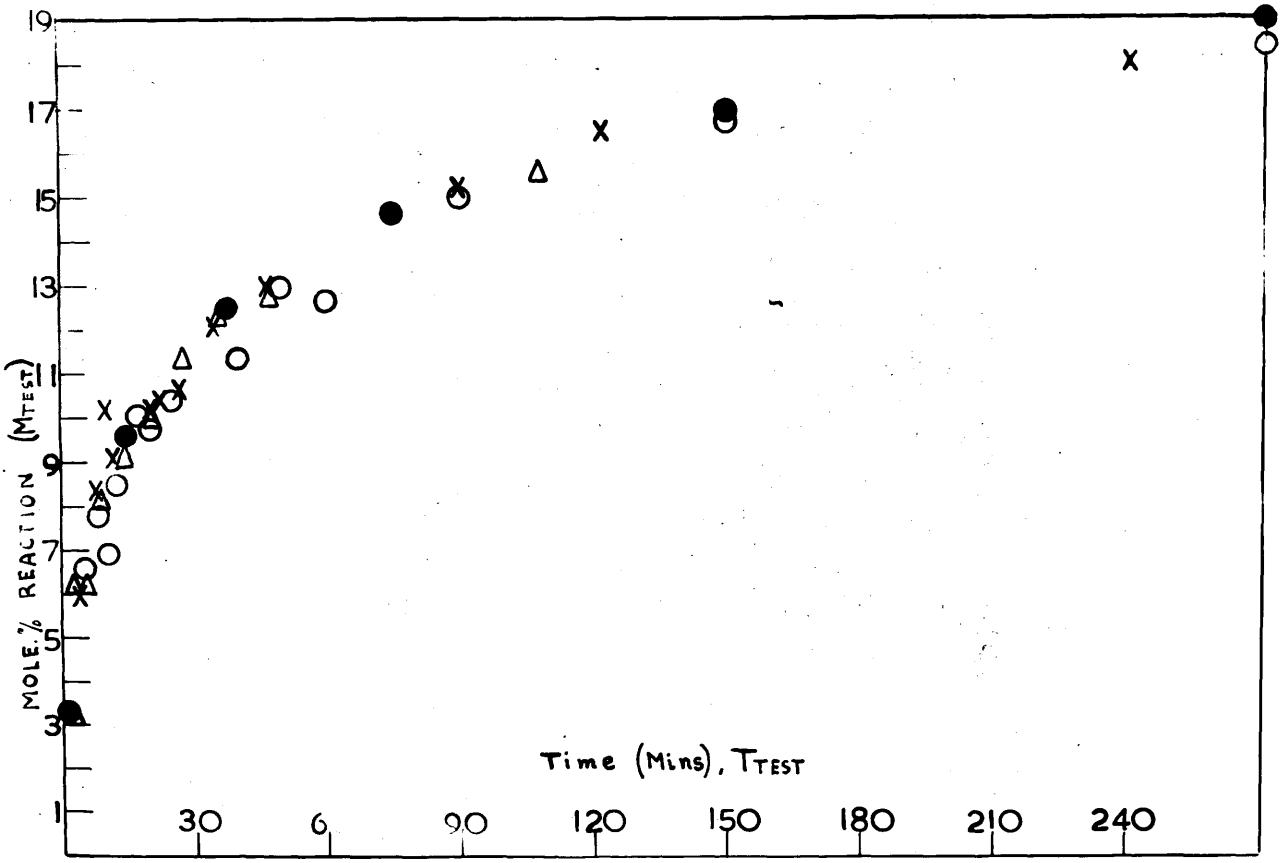
b) The reactive HCl species is maintained at a constant concentration in the aqueous phase and diffuses into the polymer particles.

Limited evidence obtained previous to the isolation of the surface reaction favoured a), but analyses of the surface reaction rate curves leave no doubt that hypothesis b) is responsible. The fact that the

range of the surface locus reaction is confined to 15-20Å from the surface is traced to the limited stability in the polymer of the diffusing reactive HCl species. The species may be interpreted as a solvated ion pair which has only a short life-time in the polymer, and which therefore can only diffuse short distances before it reacts with an unsaturated double bond or is itself decomposed by recombination to form a covalent hydrogen chloride molecule. Its random diffusion path can also carry it back into the aqueous phase before either of these two events occurs. An ion pair appears to be the most probable form of the unstable diffusing species. It is probably solvated differently from the ion pair formed within the rubber particle for the bulk reaction. Covalent hydrogen chloride molecules or separate ions are much less likely to be the reactive diffusing species.

Fig.31 embodies several kinetic tests which validate the picture of a surface reaction controlled by the hypothesis given above. The rate curve for the surface reaction of synthetic latex III at 26.7°C, 0.33 Atm HCl is taken as the reference curve (open circles). The other test points are fitted to it as follows.

1) The kinetic results for the surface reaction of synthetic latex V at 26.7°C, 0.33 Atm HCl (Fig.30, Table 30) are transformed along the y-axis by




APPLICATION OF KINETIC TEST FOR SURFACE REACTION

FIG. 31.

○ ..... SYNTHETIC LATEX III , 0·33 ATM. OF HCl, 26·7°C

X ..... SYNTHETIC LATEX V , 0·33 ATM OF HCl, 26·7°C when $M_{TEST} = M_V \times 15/22$ (TABLE 30)

Δ ..... SYNTHETIC LATEX V , 0·22 ATM. OF HCl, 26·7°C when $M_{TEST} = M_V \times 15/22$ (TABLE 31)
and $T_{TEST} = T_V \times 0.45$ (TABLE 31)

● ..... CALCULATED FROM THEORETICAL Eq. 15.

multiplying their mole % hydrochlorination by the ratio of the intercepts (P) of latex III and latex V (Fig 26), taken as 15/22 (P for latex V was actually found to be 21, Fig. 26) to provide the best fit (crosses on Fig 31). The excellent fitting by this method is in accordance with the claim that the extent of the surface reaction is proportional to the average specific surface of the particles.

2) The kinetic results for the surface reaction of latex V at 26.7°C, 0.22 Atm HCl (Fig. 30, Table 31) are shifted along both the % conversion axis, and the time axis, by multiplying the relevant mole % hydrochlorination by 15/22, and the relevant reaction time by an arbitrary factor 0.45 to obtain the best fit (triangles in Fig 31). The excellent fitting obtained by this method not only illustrates the effect of particle size as in 1), but also demonstrates that, by simply altering the time scale, the surface reaction rate curve of a latex for a particular HCl pressure can be fitted to the surface rate curve for the same latex at another pressure of HCl. This must mean that the surface hydrochlorination rate is controlled, at any given temperature, by the concentration of reactive species of HCl in the aqueous phase. More diffusing reagents are provided at the higher pressures of HCl to diffuse into the polymer. The stability in the

polymer of the HCl species is unaffected by the change in pressure. The diffusion outwards of polymer segments can therefore be discounted as this would be unaffected by changing pressure (whereas the rate is slowed down by lowering the pressure, and thus reducing the concentration of reactive species).

3) The full circles in Fig.31 are given from theoretical equation 15 derived by Dr.Gordon (see section 10.3 of this chapter).

The effect of temperature on the rate of the surface reaction is illustrated in Fig.30. Latex V was reacted at 69.5°C, at a total pressure of 0.33 Atm. The actual HCl pressure, interpolated from the International Critical Tables, was 0.22 Atm. The rate curve in the early stages (first two layers) follows closely the corresponding curve for 26.7°C, 0.22 Atm.HCl, but deviates later as the extent of the reaction increases. This effect may be ascribed to the fact, that at the higher temperature, the concentration of reactive species in the aqueous phase is unchanged (diffusion rate the same), but the stability constant $\underline{s}$ (which is a balance of rate of diffusion and decomposition) of the species in the polymer is increased. Thus, the reagents have a greater chance of penetrating further into the polymer particle to react with double bonds (thus increasing the extent of reaction). This latter experiment was carried out in co-operation with Mr.T.Carbarns who is continuing the study.

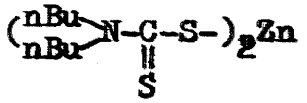
## 10.2. The Effect of Prior Vulcanization of Latex on the Hydrochlorination Reaction

Synthetic polyisoprene latices III and V were vulcanized according to the following formulations, which, along with the vulcanising dispersions, were given by Mr.C.Moss (Dunlop Rubber Co.).

TABLE 26

| | Va (gms) | Vb (gms) | = pts/100 rubber |
|---|---|---|---|
| Synthetic latex V (19.5% total solids) | 2.56 | 2.56 | - |
| 0.88 Ammonia | 0.130 | 0.130 | - |
| 50% ZnO dispersion containing 4.5% Dispersol L. | 0.006 | 0.006 | 0.60 |
| 50% S dispersion containing 3% Dispersol L. | 0.030 | 0.030 | 3.00 |
| 14.2% Aqueous Pyrogallol | - | 0.035 | 1.00 |
| These ingredients were tumbled for 3 days at 30°C before the accelerator (Butesan) was added. | | | |
| *23% Butesan dispersion containing 4.5% Dispersol L. | 0.033 | 0.033 | 1.50 |

* Butesan is zinc di-butyl-di-thio-carbamate



After storing for 7 days at room temperature, the latex was diluted and centrifuged to bring down unused reagents (especially the Butesan which is decomposed by HCl to carbon disulphide and di-Butylamine). The latex was decanted and then acidified with concentrated hydrochloric acid which arrested the vulcanization reaction. The rubber content of the latices when further diluted with water was about 5%. The above proportions of ingredients constituted a definite "overcure" by practical standards, and magnified the kinetic effects of vulcanization. The vulcanisation of latex III required only one third of the amounts of ingredients given in Table 26.

Vulcanized latices Va and Vb differed only in that pyrogallol was added to Vb, intended to act as an antioxidant. As will be seen, this had a marked effect on the surface vulcanization of Vb. As the vulcanization occurred under alkaline conditions, oxidation of pyrogallol in the latex serum took place, and became evident through the formation of the usual brown colour. The acceleration of vulcanization in latex Vb may reasonably be connected with the reactive intermediates involved in this oxidation process (e.g. free radicals).

The increase in density of the polymers caused by vulcanization has already been recorded in Table 19.

During the vulcanization period, the latices were alkaline and so special precautions were taken to prevent their oxidation. Nitrogen was used to "blanket" the latices in the reaction tubes. The fact that latices Va and Vb showed no increase from normal in their bulk hydrochlorination rate (Fig. 32) verified that no oxidation had taken place.

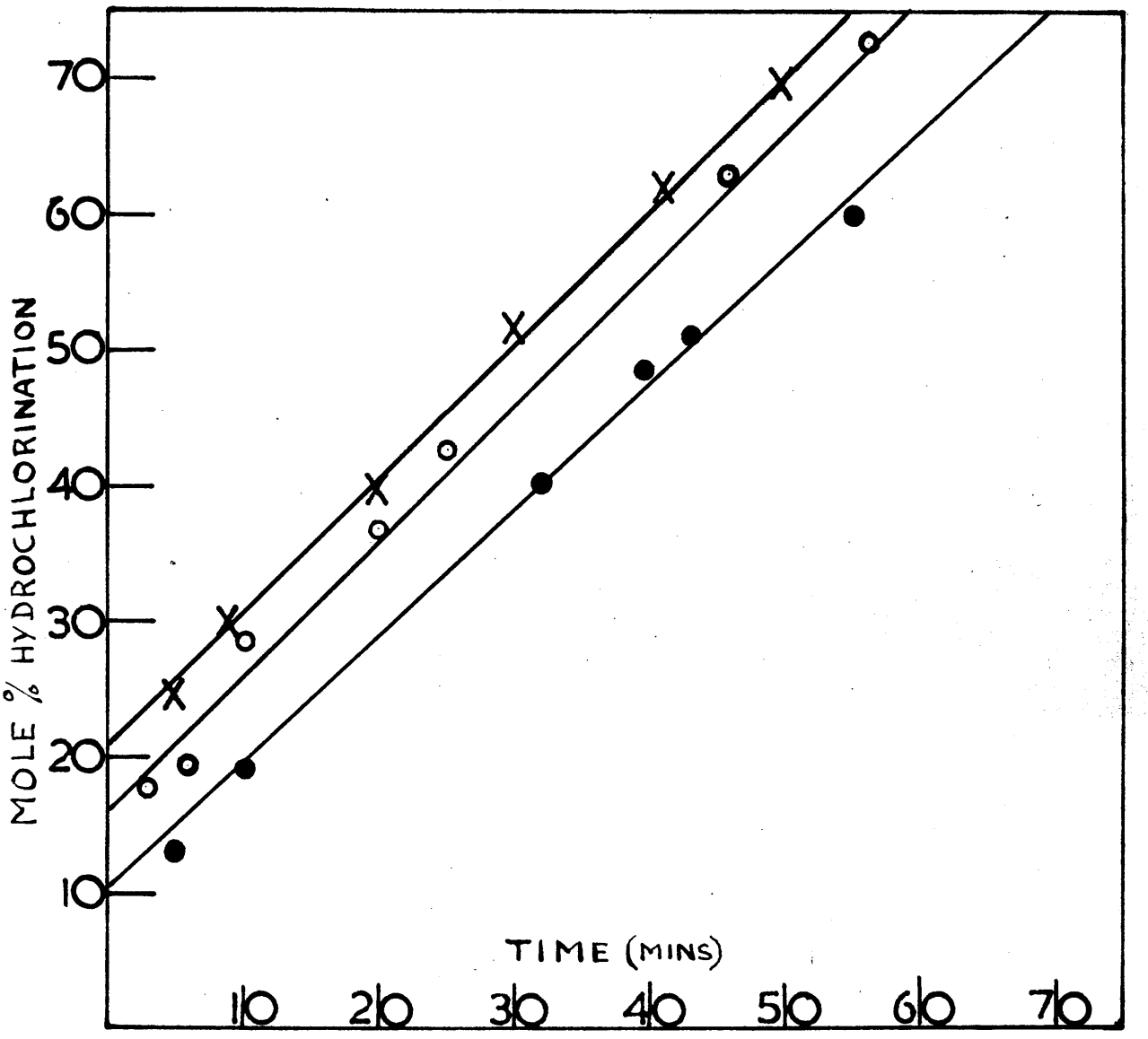
An approximate sulphur analysis of the rubber in Vb after acetone extraction, showed that practically all of the 3% sulphur had combined with the polymer. A sulphur combination of about 2.5% was also calculated from the decrease in specific volume of the purified polymer during vulcanization, viz. 0.018. (The formation of ebonite with absorption of 32% sulphur on the total weight is known to decrease the specific volume by 0.25cc/gm).

The absorption of 2-3% of sulphur would normally lead to a high state of cure with an average segment length between cross-links of 12-15 isoprene units. However, equilibrium swelling measurements in carbon tetrachloride showed that the average segment lengths were in the region of 60-100 for Va, and 110-170 for Vb. These results showed that the combined sulphur was not efficiently used in cross-linking, i.e. not evenly distributed throughout the polymer particle. The two polymers Va and Vb gave weak films after pressing at 100°C, Vb being the weaker. Film

forming properties depend on the ability of the particle surfaces to flow together, and this in turn depends on the state of cross-linking in the surface layers. It therefore seemed evident that the latices, particularly Vb, had undergone preferential surface vulcanization. This was confirmed quantitatively when the surface hydrochlorination of these latices was studied (and used as a tool to examine the state of unsaturation of the particle surface).

The effect of vulcanization on the surface hydrochlorination was first examined on latex IIIa (Fig. 29) and it was revealed that a rate reduction caused by vulcanization had taken place. The usual experimental techniques were employed to follow the reaction progress on the vulcanized synthetic latices. Electron microscope measurements showed that no change in particle size occurred during vulcanization to which changes in the rate curves could possibly be attributed.

More detailed experiments were carried out on latices Va and Vb which had a smaller average particle diameter (i.e. a surface reaction of greater proportion). These two latices were reacted at 26.7°C, 2 Atm. HCl, and the kinetic curves were compared with that of latex V (Fig 32). The slopes of the lines representing the bulk reaction rate are identical for the three latices, which shows that, as expected the bulk rate is unaffected by




HYDROCHLORINATION RATE CURVES AT 26·7°C AND 2 ATM. HCl.

FIG. 32.

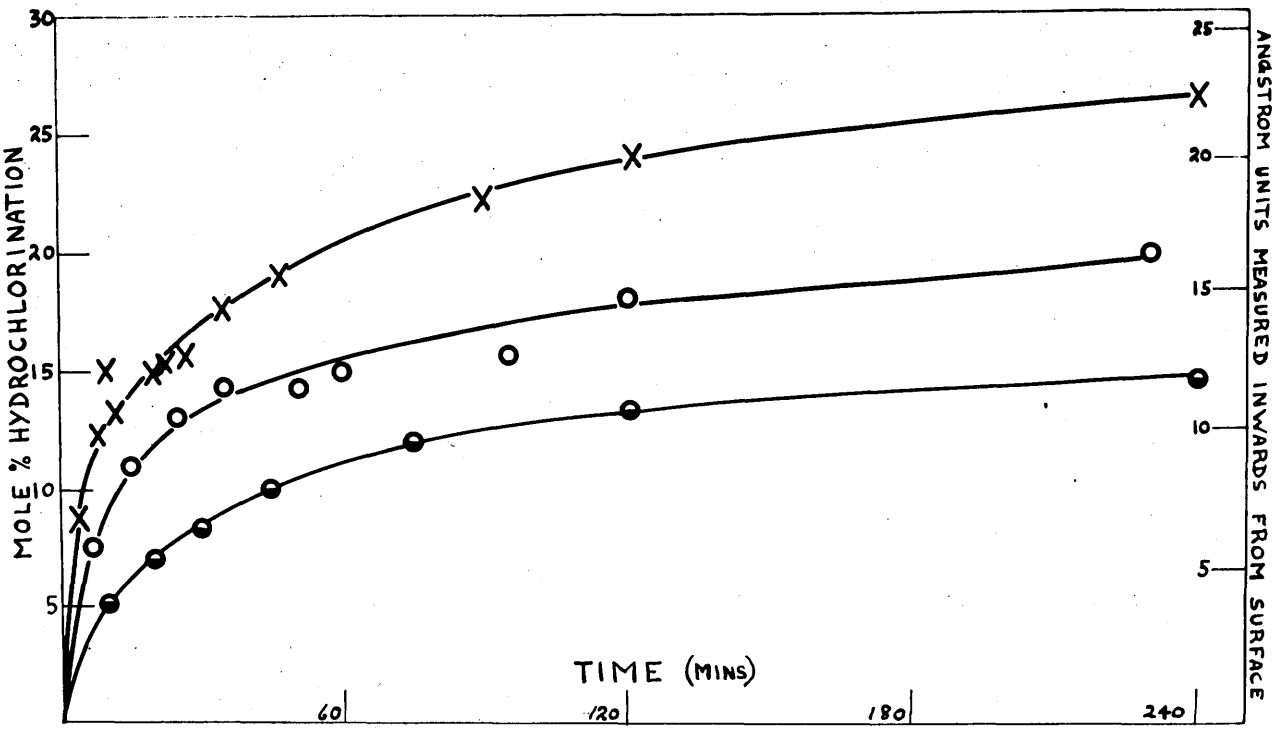
X·····UNVULCANIZED SYNTHETIC LATEX V.

O·····VULCANIZED SYNTHETIC LATEX Va.

●·····VULCANIZED SYNTHETIC LATEX Vb.

pre-vulcanization . There is, however, a parallel displacement downwards in going from latex V to Va, and a further downward displacement in going to Vb, i.e. the intercepts on the composition axis are successively reduced. In the interpretation given, the intercepts P give a measure of the available (unsaturated) units lying within the topmost 15-20Å of the particles (the outermost 3-4 molecular layers). The intercepts P for latices V, Va, and Vb are respectively 21, 16, and 10.5 Mole.% hydrochlorination from Fig.32. It appears then, that latex Va lost, through vulcanization, about 5% of the units which normally would have been available for hydrogen chloride addition in the surface reaction (i.e. one double bond in every four was deactivated in the four outermost molecular layers). Latex Vb lost about 10.5% (i.e. one double bond in every two). It was gratifying to find that polymer Vb, giving much the weaker films, was indeed also found to have the more strongly surface vulcanized particles. The loss by unsaturation amounting to 10.5% of the total unsaturation of the particles of Vb would correspond to half the double bonds in the four outermost layers, or all the double bonds in the two outer layers. The latter interpretation is supported below.

The rate curves for the surface hydrochlorination of the same three latices are illustrated




SURFACE LOCUS RATE CURVES FOR HYDROCHLORINATION AT 24·7°C, 033 ATM. HCl. FIG. 33

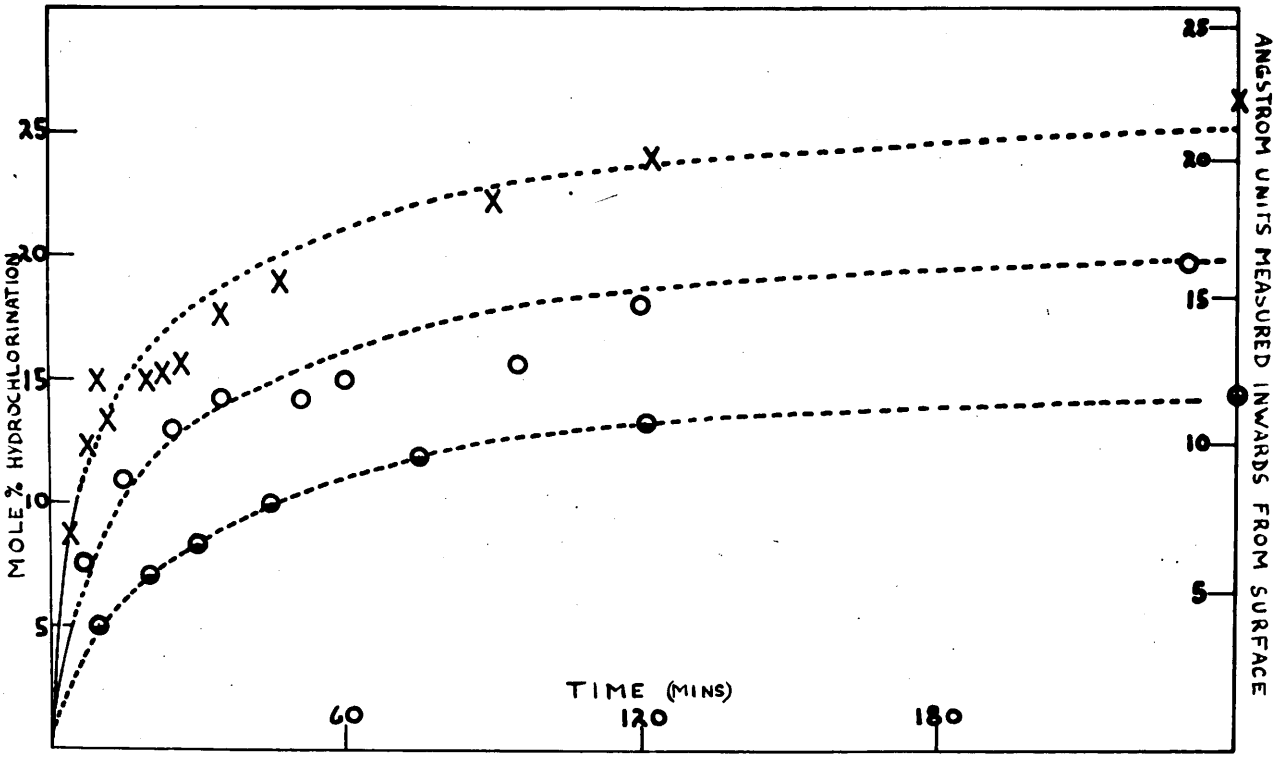
X····UNVULCANIZED SYNTHETIC LATEX V.

O····VULCANIZED SYNTHETIC LATEX Va.

⊖····VULCANIZED SYNTHETIC LATEX Vb.

in Fig 33. A reduction in rate is observed in going from V to Va to Vb. This behaviour is in complete agreement with the effect of reductions on the intercept described in the last paragraph, attributed to partial loss of unsaturation by prevulcanization of the surface unsaturation. The deceleration of the surface reaction is due to this partial loss of unsaturation.

The alternative explanation, viz. that the reduction in rate of the surface reaction is caused by hindered diffusion of the reactive HCl species, is negatived by two arguments. Firstly, the bulk rate is unaffected by vulcanization, and therefore the precursors must still be able to diffuse quickly enough into the polymer particles to maintain their equilibrium concentration there. Secondly, in comparison with unvulcanized latex V, latex Vb shows a marked reduction in the rate of hydrochlorination of the first 5% of reactive units (Fig 33), equivalent merely to the surface layer which could be reached from the aqueous phase without any diffusion through the rubber matrix. The marked reduction in rate of the surface reaction must therefore be the result of the absence, resulting from prior vulcanization, of units reactive to hydrochlorination, in the outer layer. The evidence all points to the conclusion that these units were deactivated by losing their double bonds during vulcanization. A




KINETIC TEST APPLIED TO HYDROCHLORINATION RATE CURVES
AT 26.7°C AND 0·33 ATM. HCl (DOTTED CURVES DRAWN TO BE CONGRUENT)

× UNVULCANIZED SYNTHETIC LATEX V
○ VULCANIZED SYNTHETIC LATEX Va
⊖ VULCANIZED SYNTHETIC LATEX Vb

FIG. 34

preferential vulcanization of particle surface is thus demonstrated. This would be effected by a progressive saturation from the outermost layer inwards just as happened during surface hydrochlorination.

This suggested the following kinetic check demonstrated in Fig.34. The dotted portions of the two upper curves are deliberately drawn to be congruent to the full curve of the bottom plot, i.e. the bottom plot was simply moved parallel to itself and to a new origin, to fit it to the experimentally given points of the two upper plots. The new origins are chosen by reference to the intercepts for the corresponding latices in Fig. 32, so as to be kinetically equivalent. This latter figure shows that, due to vulcanization, latex Vb lost 10.5% of its unsaturation, and latex Va lost 5%. If the amount of saturation in the surface layers controls the surface reaction rate, then it should be immaterial whether the double bonds are reactivated by vulcanization or by hydrochlorination. Therefore, the new origins to which the bottom curve is to be placed, are taken as points representing latices V and Va in an equal state of saturation as Vb, viz. 10.5%. Thus, in latex V, this amount is due entirely to hydrochlorination, in latex Va it is due to 5.5% hydrochlorination and 5% vulcanization, and in Vb, of course, entirely due to vulcanization. The subsequent rate of saturation (surface hydrochlorinat-

-ion should then be the same for each latex, and rather good concordance of the dotted portions with the actual experimental points is indeed obtained and is satisfactory considering that no adjustment of unknown parameters is made. This concordance may be taken to confirm the theory of surface vulcanization.

The equilibrium swelling measurments were carried out with small fragments of pressed polymer film. Films of unvulcanized polyisoprene dissolved completely in carbon tetrachloride, while when vulcanized, they swelled up to several times their original volume. The swelling ratios SR were found by measuring the density (density-gradient tube technique) of swollen and unswollen polymers. The swollen polymers were transferred from the carbon tetrachloride to the density-gradient tube on the point of a glass fibre. A quick spray with distilled water avoided retention on the polymer of extraneous solvent, and the transfer was performed quickly to avoid evaporation of the carbon tetrachloide taken up by the film. While this method was not refined, it was quite accurate to within the limits stated. The swelling ratio SR (volume fraction of polymer in the swollen gel) was given by;

$$SR = \frac{d_{solvent} - d_{gel}}{d_{solvent} - d_{polymer}} \qquad \text{(Eq. 13)}$$

The average molecular weight of the segment between cross-links was then obtained from the well known Flory equation;

$$M_c = \frac{2dV_o}{(SR)^{5/3}(1-2\mu)} \qquad \text{(Eq.14)}$$

where $\mu$ is an interaction constant (0.28 for rubber-$CCl_4$),

d is the density of the polymer,

$V_o$ is the molar volume of the solvent.

The average number of isoprene units between cross-links was evaluated by dividing $M_c$ by 68.

An attempt to get a cross-linked synthetic latex IV by copolymerizing isoprene with di-allyl phthalate was unsuccessful. The polymer dissolved completely in carbon tetrachloride. It appears that the two monomers do not copolymerize under the conditions used here.

The structure of the particle-aqueous acid interphase, with its adsorbed layer of stabilizer may later be found to have some bearing on the surface locus reaction. So far there has been no evidence of this, and the descriptions given in this chapter have been simplified by ignoring the subject.

## 10.3 Theoretical Rate Equation for Surface Hydrochlorination

A theoretical rate equation for the

surface hydrochlorination reaction has been derived by Dr.M.Gordon. His diffusion theory envisages the diffusion into the polymer particle of the unstable HCl species to proceed by a series of jumps (due to Brownian movement) from one lattice site to another. The solution is smoothed by a novel device consisting of solving differential equations containing an infinite number of rate constants (one for each lattice layer), and each constant is derived from a discontinuous (jump) model. The diffusion process is considered as one-dimensional (reagent moving in straight line into particle), and he has shown that lateral diffusion may be neglected since it is small and constant. The diffusing species is taken up (as described above) at reactive sites (double bonds) which then become deactivated and unreactive towards any further diffusing reagent arriving there. The unstable species may,of course, decompose or return (in backward jumps) to the aqueous "bath" before arriving at an unreacted site.

Gordon's rate equation is;

$$H = \sum_{i=1}^{\infty}\left\{\left(\sum_{a=1}^{\infty} C_{a,i,s}\right)\left(1-e^{-k_{i,s}\cdot t}\right)\right\} \qquad \text{(Eq.15)}$$

Where H is a measure of hydrochlorination, expressed in units such that the complete hydrochlorination of one polymer layer is given by H=1.

k is the rate constant for the ath lattice layer (k=1 for the surface layer)

s is a stability constant (the chance of the reactive species surviving a jump from one lattice site to the next).

C is a coefficient.

i is a constant.

t is time.

Some information must be "fed into" Eq.15, viz. the spacing of the polymer chain layers. Thus, in the case given below, where the theory is fitted to the experimental results for the surface reaction of synthetic latex III (Fig.31), the spacing between molecular layers is taken as 5Å. The average particle diameter of latex III is known to be 670Å (Table 20). Putting $\underline{t}=5$ and $D=670$ in Eq.8, we get P, the corresponding actual mole.% hydrochlorination, equal to 4.5%. H=1 is then equivalent to 4.5%. Thus by multiplying the values of H, in column 2 of Table 27 below, by 4.5, the actual % conversion which has occurred in the surface reaction is found. This amount of hydrochlorination has not taken place wholly in the first four molecular layers, but any conversion caused by diffusion of the reactive species further inwards than the 8th layer is negligible, i.e. 8 layers are considered in this case for equation 15.

The theoretical results for Fig.31 are obtained then from equation 15 by considering the first 8 molecular layers and taking $\underline{s}=0.4649$, so that we get,

$$H = 0.71523(1-e^{-t}) + 0.90538(1-e^{-0.23246t})$$
$$+ 0.97412(1-e^{-0.05712t}) + 0.99228(1-e^{-0.01408t})$$
$$+ 0.99603(1-e^{-0.00347t}) + 1.00000(1-e^{-0.00086t})$$
$$+ 0.99400(1-e^{-0.00021t}) + 0.98300(1-e^{-0.00005t})$$

and the results are tabulated as

Table 27

| t | H | Mole.% Reaction(H x 4.5) | T (=t x 1.5) (mins) |
|---|---|---|---|
| 1 | 0.7176 | 3.23 | 1.5 |
| 10 | 2.1315 | 9.59 | 15.0 |
| 25 | 2.7620 | 12.43 | 37.5 |
| 50 | 3.2540 | 14.60 | 75.0 |
| 100 | 3.7420 | 16.84 | 150.0 |
| 200 | 4.2240 | 19.00 | 300.0 |

t is multiplied by an arbitrary constant 1.5, to adjust the results of M to the correct time scale. The figures in columns 3 and 4 are plotted in Fig.31, and fit excellently on the experimental curve for latex III.

The mathematical theory from which these results have been obtained is to be published by Dr. M. Gordon.

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## CONCLUSIONS

The normal stability of rubber is due mainly to its properties as a poor solvent for polar substances rather than to any inherent chemical stability. It is, in fact, an exceedingly reactive substance. Cyclization and hydrochlorination in latex have shown that certain polar reagents ($H_3SO_4^+$ and $H^+,Cl^-$) react instantaneously with the unsaturation in rubber, and these reagents are available in relatively mild aqueous solutions. The difficulty in solution chemistry of rubber lies in finding common solvent media for the rubber hydrocarbon and the polar reagents.

The significance of latex chemistry is illustrated by the presence of bulk and surface reaction loci, and the control of apparent chemical reactivity by the actual solvent properties of the polymer substance. The role of particle size in latex reactions may be stressed, since, the smaller the particle, the nearer to the would-be substrate come the polar reagents.

Kinetic studies are the most effective tool for the understanding of reaction loci. The kinetics of latex reactions can give structural information about the polymer and its reactions if the polymer is involved in the rate-controlling step, or colloid-chemical information if a step can be isolated from which the

polymer is excluded.

There is much scope for further studies on rubber latex reactions, and many methods of approaching the subject to obtain a clearer comprehensive understanding of such reactions present themselves. The study of the surface effect may be extended by catalytic hydrogenation of the surface layers, akin to vulcanization, and by examining particles of very much smaller size. By hydrochlorinating latex which contains some sulphuric acid in the serum, some insight into the effect of concentration and HCl activity may be gained. Hydrochlorination of partly cyclized rubber latex, and of other rubber latex species could yield interesting results for comparison with those reported in this thesis. The importance of degradative studies has already been noted. Several of those topics are already under investigation in these laboratories.

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## APPENDIX

### Tables of Experimental Results for Graphical Figures.

N.B. All density and specific volume measurements recorded in the tables were determined at 26.7°C.

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | |
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| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| 13.8. | | " | 2.40726 | " | | |
| 14.11. | | " | 2.00300 | " | | |

Column 4 above then converted to per cent hydrochlorination, and related to specific volume for Figs. 1 and 2.

| Sample | Density (d) at 26.7°C. | Specific Volume (V) | Mole.% Reaction (M) | M |
|---|---|---|---|---|
| 11.1. | 0.9209 ± .0004 | 1.086 | 6.72 | |
| 13.2. | 0.9311 ± .0010 | 1.074 | 7.95 | 1 |
| 13.3. | 0.9314 ± .0010 | 1.071 | 9.91 | 1 |
| 13.4. | 0.9384 ± .0008 | 1.065 | 11.80 | 2 |
| | | | | |
| | | | | |
| | | | | |

Table 1. (figures 1 and 2)

Relationship between specific volume and per cent conversion of partially hydrochlorinated Hevea rubber, obtained from density measurements and potentiometric titrations.

| Sample | Weight of Polymer | Weight of $AgNO_3$ soln. | Wt.% Chlorine in Polymer (C) |
|---|---|---|---|
| 1F.1. | 34.55 mgm | 0.68081 gm | 3.37±.05 |
| 1E.2. | 19.22 " | 0.46053 " | 3.94 .05 |
| 1E.3. | 51.32 " | 1.49660 " | 4.90 .05 |
| 1E.4. | 83.25 " | 3.53565 " | 7.14 .05 |
| 1E.5. | 17.44 " | 0.95091 " | 9.15 .05 |
| 1R.1. | 22.58 " | 1.23300 " | 9.20 .05 |
| 1G.2. | 24.65 " | 2.12225 " | 14.68 .05 |
| 1N.3. | 35.15 " | 3.60400 " | 17.28 .03 |
| 1G.3. | 33.53 " | 3.95404 " | 19.90 .05 |
| 1G.4. | 22.58 " | 3.04533 " | 22.68 .08 |
| 1J.3. | 31.44 " | 4.65600 " | 24.96 .03 |
| 1G.5. | 12.43 " | 2.08517 " | 28.17 .05 |
| 1E.6. | 14.48 " | 2.57375 " | 29.90 .08 |
| 1R.2. | 10.02 " | 1.88500 " | 31.28 .10 |
| 1E.7. | 13. 25 " | 2.49797 " | 31.75 .10 |
| 1Ø.1. | 12.34 " | 2.33060 " | 31.81 .05 |
| 1Ø.3. | 8.51 " | 1.61784 " | 31.97 .05 |
| 1Ø.5. | 10.25 " | 1.95280 " | 32.07 .03 |
| 1E.8. | 12.73 " | 2.40726 " | 32.13 .08 |
| 1Q.11. | 21.20 " | 4.08300 " | 32.48 .05 |

Column 4 above then converted to per cent hydrochlorination, and related to specific volume for Figs. 1 and 2.

| Sample | Density (d) at 26.7°C. | Specific Volume (V) | Mole.% Reaction (M) | Wt.% Reaction (W) |
|---|---|---|---|---|
| 1F.1. | 0.9209±.0004 | 1.086 | 6.72 | 9.95 |
| 1E.2. | 0.9311 .0010 | 1.074 | 7.95 | 11.62 |
| 1E.3. | 0.9334 .0010 | 1.071 | 9.91 | 14.44 |
| 1E.4. | 0.9464 .0008 | 1.057 | 14,80 | 21.06 |
| 1E.5. | 0.9638 .0010 | 1.038 | 19.41 | 27.00 |
| 1R.1. | 0.9552 .0010 | 1.047 | 19.53 | 27.14 |
| 1G.2. | 0.9944 .0002 | 1.006 | 33.21 | 43.30 |

Table 1 (contd.) (figures 1 and 2)

| Sample | Density (d) at 26.7°C. | Specific Volume (V) | Mole.% Reaction (M) | Wt.% Reaction (W) |
|---|---|---|---|---|
| 1N.3. | 1.0131±.0002 | 0.9874 | 40.40 | 50.90 |
| 1G.3. | 1.0296 .0005 | 0.9709 | 48.08 | 58.65 |
| 1G.4. | 1.0508 .0006 | 0.9515 | 56.85 | 66.90 |
| 1J.3. | 1.0726 .0004 | 0.9320 | 64.68 | 73.60 |
| 1G.5. | 1.1028 .0005 | 0.9067 | 76.25 | 83.10 |
| 1E.6. | 1.1214 .0004 | 0.8917 | 83.00 | 88.20 |
| 1R.2. | 1.1412 .0010 | 0.8764 | 88.65 | 92.35 |
| 1E.7. | 1.1465 .0008 | 0.8720 | 90.63 | 93.67 |
| 1Ø.1. | 1.1485 .0004 | 0.8706 | 90.84 | 93.83 |
| 1Ø.3. | 1.1477 .0010 | 0.8716 | 91.56 | 94.32 |
| 1Ø.5. | 1.1517 .0008 | 0.8682 | 92.00 | 94.58 |
| 1E.8. | 1.1518 .0005 | 0.8682 | 92.20 | 94.75 |
| 1Q.11. | 1.1535 .0010 | 0.8665 | 93.70 | 95.80 |

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TABLE 6 (Figure 16)

Experimental results for the hydrochlorination of Hevea latex at 1 Atm. of HCl and 26.7 °C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 1V.1. | 5m | 0.9064 ± .0003 | 1.103 | 0.75 |
| 1V.6. | 11.5m | 0.9096 .0005 | 1.099 | 1.75 |
| 1V.2. | 15m | 0.9106 .0002 | 1.098 | 2.00 |
| IV.4. | 22.5m | 0.9130 .0004 | 1.095 | 3.20 |
| 1V.3. | 30m | 0.9142 .0005 | 1.094 | 3.30 |
| 1K.1. | 30m | 0.9136 .0005 | 1.094 | 3.30 |
| 1V.5. | 37.5m | 0.9146 .0005 | 1.093 | 3.75 |
| 1X.1. | 1hr 15m | 0.9178 .0005 | 1.090 | 4.50 |
| 1B.2. | 1hr 27m | 0.9203 .0010 | 1.087 | 5.50 |
| 1F.1. | 1hr 30m | 0.9209 .0004 | 1.086 | 5.75 |
| 1J.1. | 2hr 20m | 0.9235 .0004 | 1.082 | 7.00 |
| 1B.3. | 3hr 5m | 0.9258 .0002 | 1.080 | 7.50 |
| 1C.2. | 3hr 25m | 0.9274 .0030 | 1.078 | 8.10 |
| 1E.3. | 4hr | 0.9334 .0010 | 1.071 | 10.25 |
| 1T.2. | 4hr 20m | 0.9321 .0004 | 1.073 | 9.75 |
| 1A.1. | 4hr 50m | 0.9365 .0005 | 1.068 | 11.25 |
| 1T.3. | 5hr 30m | 0.9380 .0004 | 1.066 | 11.90 |
| 1X.2. | 5hr 30m | 0.9408 .0010 | 1.063 | 12.75 |
| 1U.1. | 6hr 30m | 0.9411 .0002 | 1.063 | 12.75 |
| 1B.4. | 7hr 10m | 0.9470 .0002 | 1.056 | 15.00 |
| 1E.4. | 7hr 25m | 0.9464 .0008 | 1.056 | 15.00 |
| 1T.5. | 8hr | 0.9551 .0005 | 1.047 | 17.25 |
| 1M.2. | 8hr 30m | 0.9530 .0004 | 1.049 | 16.50 |
| 1T.6. | 9hr | 0.9624 .0005 | 1.040 | 19.25 |
| 1X.4. | 10hr | 0.9732 .0005 | 1.028 | 23.25 |
| 1T.8. | 10hr | 0.9720 .0008 | 1.029 | 23.00 |
| 1X.5. | 10hr 30m | 0.9741 .0008 | 1.027 | 24.00 |
| 1T.9. | 10hr 30m | 0.9746 .0002 | 1.026 | 24.50 |
| 1U.2. | 11hr 30m | 0.9816 .0005 | 1.018 | 27.25 |
| 1N.1. | 11hr 30m | 0.9707 .0010 | 1.030 | 22.50 |
| 1U.3. | 12hr | 0.9878 .0004 | 1.012 | 29.75 |
| 1Y.1. | 12hr | 0.9844 .0010 | 1.016 | 28.50 |
| 1D.1. | 12hr 10m | 0.9818 .0020 | 1.018 | 27.25 |
| 1N.2. | 13hr | 0.9874 .0006 | 1.013 | 29.50 |
| 1U.4. | 14hr | 1.0112 .0004 | 0.988 | 39.50 |
| 1D.2. | 14hr 20m | 0.9931 .0010 | 1.007 | 32.00 |
| 1U.5. | 15hr | 1.0256 .0002 | 0.975 | 45.80 |
| 1Z.1. | 15hr 5m | 1.0290 .0010 | 0.972 | 47.50 |
| 1N.3. | 15hr 30m | 1.0131 .0002 | 0.987 | 40.60 |
| LD.3. | 16hr 18m | 1.0217 .0008 | 0.979 | 44.50 |
| 1N.4. | 17hr | 1.0340 .0005 | 0.967 | 49.40 |
| 1C.3. | 17hr 38m | 1.0485 .0005 | 0.954 | 55.50 |
| 1U.6. | 18hr | 1.0649 .0005 | 0.939 | 61.75 |
| 1C.4. | 18hr 30m | 1.0610 .0010 | 0.943 | 60.20 |

TABLE 6

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 1O.1. | 18hr 45m | 1.0592 ± .0008 | 0.944 | 59.40 |
| 1D.4. | 19hr 30m | 1.0636 .0010 | 0.940 | 61.60 |
| 1U.7. | 20hr | 1.0935 .0004 | 0.914 | 72.50 |
| 1X.2. | 20hr | 1.1017 .0010 | 0.908 | 75.50 |
| 1W.1. | 20hr 30m | 1.1002 .0010 | 0.909 | 74.90 |
| 1Q.1. | 20hr 35m | 1.0930 .0010 | 0.915 | 72.25 |
| 1Z.3. | 21hr | 1.1130 .0005 | 0.898 | 79.50 |
| 1O.2. | 21hr 35m | 1.1004 .0010 | 0.9090 | 74.90 |
| 1Z.4. | 22hr | 1.1237 .0005 | 0.890 | 83.25 |
| 1C.5. | 22hr 13m | 1.1076 .0004 | 0.903 | 77.70 |
| 1Q.2. | 23hr | 1.1265 .0005 | 0.888 | 83.80 |
| 1W.3. | 23hr 30m | 1.1335 .0010 | 0.882 | 86.50 |
| 1B.5. | 23hr 50m | 1.1366 .0002 | 0.880 | 87.50 |
| 1J.6. | 24hr | 1.1403 .0008 | 0.877 | 88.60 |
| 1W.4. | 24hr | 1.1370 .0005 | 0.880 | 87.50 |
| 1Q.3. | 24hr 20m | 1.1408 .0008 | 0.876 | 88.80 |
| 1W.5. | 24hr 30m | 1.1401 .0005 | 0.877 | 88.75 |
| 1W.6. | 25hr | 1.1462 .0005 | 0.872 | 90.75 |
| 1Q.4. | 25hr | 1.1469 .0010 | 0.872 | 90.75 |
| 1W.7. | 25hr 30m | 1.1448 .0008 | 0.874 | 90.00 |
| 1Q.5. | 26hr 20m | 1.1462 .0003 | 0.873 | 90.50 |
| 1W.9. | 26hr 30m | 1.1462 .0008 | 0.873 | 90.50 |
| 1W.10. | 27hr | 1.1465 .0008 | 0.872 | 90.75 |
| 1ø.1. | 27 hr | 1.1485 .0008 | 0.871 | 91.00 |
| 1E.7. | 27hr 30m | 1.1444 .0004 | 0.874 | 90.00 |
| 1W.11. | 27hr 45m | 1.1462 .0010 | 0.872 | 90.75 |
| 1ø.3. | 30hr | 1.1477 .0010 | 0.871 | 91.00 |
| 1Q.6. | 29hr 30m | 1.1480 .0010 | 0.871 | 91.00 |
| 1E.8. | 30hr 30m | 1.1465 .0008 | 0.872 | 90.75 |
| 1ø.4. | 31hr | 1.1497 .0004 | 0.870 | 91.50 |
| 1Q.7. | 31hr 30m | 1.1529 .0010 | 0.870 | 91.50 |
| 1ø.5. | 32hr | 1.1517 .0007 | 0.868 | 92.50 |
| 1B.6. | 32hr 45m | 1.1513 .0010 | 0.868 | 92.50 |
| 1Q.8. | 33hr | 1.1515 .0010 | 0.868 | 92.50 |
| 1D.5. | 41hr 23m | 1.1509 .0010 | 0.869 | 92.25 |
| 1Q.9. | 47hr | 1.1535 .0010 | 0.866 | 93.25 |
| 1B.7. | 48hr 40m | 1.1526 .0010 | 0.867 | 93.00 |
| 1B.8. | 53hr 35m | 1.1537 .0010 | 0.866 | 93.25 |
| 1Q.10. | 69hr | 1.1537 .0005 | 0.866 | 93.25 |
| 1Q.11. | 77hr 20m | 1.1537 .0010 | 0.866 | 93.25 |

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TABLE 7 (Figure 17)

Experimental results for the hydrochlorination of Hevea latex at 1 Atm. of HCl and 0°C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 2H.2. | 23m | 0.9096±.0004 | 1.099 | 1.75 |
| 2C.1. | 30m | 0.9150 .0005 | 1.093 | 3.75 |
| 2E.1. | 45m | 0.9142 .0004 | 1.094 | 3.40 |
| 2G.3. | 1hr | 0.9171 .0010 | 1.091 | 4.25 |
| 2C.2. | 1hr 20m | 0.9240 .0002 | 1.082 | 7.00 |
| 2G.4. | 1hr 30m | 0.9242 .0010 | 1.082 | 7.00 |
| 2C.3. | 1hr 50m | 0.9288 .0002 | 1.076 | 8.75 |
| 2G.5. | 1hr 50m | 0.9269 .0002 | 1.079 | 7.90 |
| 2J.3. | 2hr | 0.9327 .0006 | 1.072 | 10.00 |
| 2F.1. | 2hr 30m | 0.9315 .0002 | 1.073 | 9.80 |
| 2J.4. | 2hr 35m | 0.9379 .0004 | 1.066 | 12.00 |
| 2F.2. | 3hr | 0.9380 .0002 | 1.066 | 12.00 |
| 2J.5. | 3hr | 0.9444 .0006 | 1.059 | 14.00 |
| 2F.3. | 3hr 30m | 0.9448 .0002 | 1.058 | 14.25 |
| 2F.4. | 4hr | 0.9565 .0010 | 1.045 | 18.00 |
| 2J.6. | 4hr | 0.9628 .0006 | 1.039 | 20.00 |
| 2C.4. | 4hr 15m | 0,9748 .0010 | 1.026 | 24.50 |
| 2G.6. | 4hr 26m | 0.9728 .0020 | 1.028 | 23.50 |
| 2C.5. | 5hr | 0.9958 .0005 | 1.004 | 33.50 |
| 2J.7. | 5hr | 0.9920 .0002 | 1.008 | 31.50 |
| 2C.6. | 5hr 30m | 1.0130 .0002 | 0.987 | 41.00 |
| 2G.7. | 5hr 32m | 1.0044 .0002 | 0.996 | 37.00 |
| 2C.7. | 6hr 15m | 1.0344 .0002 | 0.967 | 49.50 |
| 2G.8. | 6hr 30m | 1.0355 .0002 | 0.965 | 50.50 |
| 2G.9. | 7hr | 1.0576 .0002 | 0.945 | 59.00 |
| 2C.8. | 7hr 15m | 1.0714 .0010 | 0.934 | 64.00 |
| 2G.10. | 7hr 30m | 1.0710 .0004 | 0.934 | 64.00 |
| 2F.5. | 8hr | 1.0787 .0002 | 0.928 | 66.50 |
| 2F.6. | 8hr 30m | 1.0913 .0003 | 0.917 | 71.50 |
| 2F.7. | 9hr | 1.0985 .0008 | 0.909 | 75.00 |
| 2C.9. | 9hr | 1.1048 .0005 | 0.905 | 76.50 |
| 2B.1. | 9hr 30m | 1.1048 .0010 | 0.905 | 76.50 |
| 2N.1. | 9hr 30m | 1.1077 .0020 | 0.903 | 77.40 |
| 2F.8. | 9hr 45m | 1.1062 .0010 | 0.9050 | 76.50 |
| 2N.2. | 10hr | 1.1096 .0020 | 0.901 | 78.25 |
| 2F.9. | 10hr 30m | 1.1115 .0010 | 0.898 | 79.50 |
| 2N.3. | 10hr 30m | 1.1109 .0020 | 0.900 | 78.75 |
| 2K.1. | 11hr 40m | 1.1090 .0003 | 0.902 | 77.80 |
| 2K.2. | 12hr 10m | 1.1116 .0020 | 0.899 | 79.00 |
| 2K.3. | 12hr 40m | 1.1116 .0008 | 0.899 | 79.00 |
| 2K.5. | 14hr 40m | 1.1202 .0020 | 0.893 | 81.75 |
| 2K.6. | 17hr 10m | 1.1214 .0020 | 0.892 | 82.25 |
| 2K.7. | 18hr 15m | 1.1192 .0020 | 0.894 | 81.40 |

TABLE 7

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 2L.1. | 22hr | 1.1252 ± .0010 | 0.889 | 83.50 |
| 2N.4. | 24hr | 1.1270 .0010 | 0.888 | 83.80 |
| 2N.5. | 26hr 30m | 1.1326 .0020 | 0.883 | 86.00 |
| 2N.6. | 28hr 25m | 1.1356 .0020 | 0.881 | 87.00 |
| 2N.7. | 30hr | 1.1339 .0010 | 0.882 | 86.50 |
| 2N.8. | 47hr 30m | 1.1356 .0010 | 0.881 | 87.00 |
| 2N.9. | 52hr 45m | 1.1424 .0010 | 0.876 | 89.00 |
| 2N.10. | 60hr | 1.1436 .0010 | 0.875 | 89.50 |

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TABLE 8 (Figure 18)

Experimental results for the hydrochlorination of Hevea latex at 1 Atm.total pressure, 0.91 Atm.of HCl and 69.5°C.

| | | | | |
|---|---|---|---|---|
| 3G.1. | 30m | 0.9185 ± .0004 | 1.088 | 5.00 |
| 3C.1. | 1hr | 0.9196 .0004 | 1.087 | 5.50 |
| 3G.2. | 1hr 15m | 0.9231 .0008 | 1.083 | 6.75 |
| 3G.3. | 1hr 50m | 0.9254 .0010 | 1.081 | 7.40 |
| 3A.1. | 2hr | 0.9256 .0004 | 1.080 | 7.50 |
| 3G.4. | 2hr 30m | 0.9266 .0008 | 1.079 | 7.90 |
| 3G.5. | 3hr | 0.9330 .0010 | 1.072 | 10.00 |
| 3A.2. | 3hr | 0.9271 .0002 | 1.079 | 7.90 |
| 3C.2. | 4hr 5 m | 0.9295 .0005 | 1.075 | 9.00 |
| 3C.3. | 4hr 50m | 0.9336 .0010 | 1.071 | 10.25 |
| 3C.4. | 6hr 40m | 0.9366 .0002 | 1.067 | 11.60 |
| 3C.5. | 9hr 5m | 0.9444 .0004 | 1.059 | 14.00 |
| 3C.6. | 10hr | 0.9484 .0005 | 1.055 | 15.00 |
| 3F.1. | 11hr 49m | 0.9523 .0004 | 1.050 | 16.50 |
| 3B.1. | 13hr 20m | 0.9540 .0010 | 1.048 | 17.25 |
| 3F.3. | 13hr 45m | 0.9566 .0002 | 1.045 | 18.00 |
| 3B.2. | 14hr 6m | 0.9572 .0002 | 1.045 | 18.00 |
| 3F.5. | 16hr 5m | 0.9600 .0010 | 1.042 | 19.00 |
| 3F.4. | 14hr 45m | 0.9558 .0004 | 1.046 | 17.75 |
| 3B.3. | 15hr | 0.9602 .0006 | 1.042 | 19.00 |
| 3B.4. | 16hr 50m | 0.9668 .0006 | 1.035 | 21.75 |
| 3F.6. | 17hr | 0.9630 .0005 | 1.038 | 20.25 |
| 3D.1. | 17hr 5m | 0.9636 .0010 | 1.037 | 20.50 |
| 3E.1. | 17hr 30m | 0.9664 .0008 | 1.035 | 21.25 |
| 3F.7. | 18hr 20m | 0.9681 .0005 | 1.033 | 22.00 |
| 3B.5. | 18hr 45m | 0.9741 .0030 | 1.027 | 24.00 |
| 3F.8. | 19hr 25m | 0.9725 .0005 | 1.028 | 23.50 |
| 3F.9. | 20hr | 0.9741 .0005 | 1.027 | 24.00 |
| 3B.7. | 21hr | 0.9837 .0004 | 1.016 | 28.25 |
| 3C.7. | 23hr 35m | 0.9981 .0006 | 1.001 | 34.80 |
| 3C.8. | 24hr 35m | 1.0077 .0010 | 0.993 | 38.50 |
| 3C.9. | 25hr 25m | 1.0105 .0004 | 0989 | 40.00 |
| 3C.10. | 26hr | 1.0142 .0008 | 0.987 | 41.00 |
| 3C.11. | 28hr 25m | 1.0274 .0008 | 0.974 | 46.50 |
| 3C.12. | 30hr | 1.0379 .0005 | 0.964 | 51.00 |

TABLE 9 (Figure 19)

Experimental results for the hydrochlorination of Hevea latex at 2 Atm. of HCl and 26.7°C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 4P.1. | 15m | 0.9222±.0010 | 1.085 | 6.25 |
| 4P.2. | 23m | 0.9259 .0002 | 1.080 | 7.50 |
| 4P.3. | 30m | 0.9380 .0010 | 1.066 | 11.80 |
| 4P.4. | 37.5m | 0.9368 .0003 | 1.067 | 11.50 |
| 4P.5. | 45m | 0.9428 .0004 | 1.060 | 13.60 |
| 4P.6. | 60m | 0.9608 .0005 | 1.041 | 19.40 |
| 4P.7. | 62m | 0.9552 .0005 | 1.047 | 17.75 |
| 4P.8. | 65m | 0.9656 .0010 | 1.035 | 21.25 |
| 4P.9. | 67m | 0.9685 .0010 | 1.032 | 22.20 |
| 4P.10. | 70m | 0.9782 .0003 | 1.022 | 25.50 |
| 4P.11. | 72m | 0.9791 .0001 | 1.021 | 26.00 |
| 4P.12. | 75m | 0.9918 .0015 | 1.008 | 31.50 |
| 4P.13. | 80m | 0.9986 .0005 | 1.002 | 34.50 |
| 4P.14. | 90m | 1.0176 .0010 | 0.983 | 42.50 |
| 4P.15. | 97m | 1.0268 .0002 | 0.9740 | 46.50 |
| 4P.16. | 105m | 1.0482 .0008 | 0.9540 | 55.00 |
| 4P.17. | 120m | 1.0820 .0002 | 0.924 | 68.25 |
| 4P.18. | 130m | 1.0836 .0004 | 0.922 | 69.00 |
| 4P.19. | 135m | 1.0967 .0010 | 0.911 | 74.00 |
| 4P.20. | 150m | 1.1204 .0010 | 0.893 | 81.50 |
| 4P.21. | 165m | 1.1358 .0008 | 0.881 | 87.20 |
| 4P.22. | 195m | 1.1459 .0010 | 0.873 | 90.40 |
| 4P.23. | 300m | 1.1458 .0010 | 0.873 | 90.40 |

TABLE 10 (Figure 19)

Freedom of reaction rate from chance effects (examined at 2 Atm.HCl and 26.7°C.).

| | | | | |
|---|---|---|---|---|
| | | 4.5% Vulcastab L.W. in latex | | |
| 5P.1. | 90m | 0.9992 .0005 | 1.001 | 34.75 |
| 5P.2. | 107m | 1.0520 .0005 | 0.951 | 56.70 |
| 5P.3. | 120m | 1.0700 .0005 | 0.935 | 63.70 |
| 5P.4. | 130m | 1.0990 .0005 | 0.910 | 74.00 |
| | | Latex creamed for 24 hours (alkaline conditions) | | |
| 6P.1. | 65m | 0.9694 .0003 | 1.032 | 21.60 |
| 6P.2. | 90m | 1.0084 .0005 | 0.993 | 38.30 |
| 6P.3. | 100m | 1.0300 .0010 | 0.971 | 47.75 |
| 6P.4. | 123m | 1.0860 .0005 | 0.920 | 69.90 |
| | | Revertex latex | | |
| 7P.1. | 85m | 1.0082 .0002 | 0.993 | 38.30 |
| 7P.2. | 105m | 1.0644 .0020 | 0.938 | 61.00 |

TABLE 11 (Figure 20)

Experimental results for the hydrochlorination of Hevea latex at 2 Atm. of HCl and 0°C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 8P.1. | 5m | 0.9140 ± .0010 | 1.094 | 3.40 |
| 8P.2. | 10m | 0.9196 .0005 | 1.087 | 5.50 |
| 8P.3. | 15m | 0.9282 .0008 | 1.078 | 8.20 |
| 8P.4. | 18m | 0.9406 .0010 | 1.063 | 12.75 |
| 8P.5. | 20m | 0.9556 .0015 | 1.046 | 18.00 |
| 8P.6. | 22½m | 0.9811 .0004 | 1.019 | 27.50 |
| 8P.7. | 25m | 1.0045 .0005 | 0.996 | 37.00 |
| 8P.8. | 35m | 1.0790 .0020 | 0.9264 | 67.20 |
| 8P.9. | 30m | 1.0264 .0005 | 0.9749 | 46.00 |
| 8P.10. | 32½m | 1.0510 .0002 | 0.952 | 56.25 |
| 8P.11. | 40m | 1.0936 .0008 | 0.914 | 72.50 |
| 8P.12. | 42½m | 1.0954 .0010 | 0.913 | 73.10 |
| 8P.13. | 45m | 1.1147 .0010 | 0.897 | 80.00 |
| 8P.14. | 52½m | 1.1177 .0010 | 0.895 | 81.00 |
| 8P.15. | 60m | 1.1192 .0010 | 0.894 | 81.50 |
| 8P.16. | 120m | 1.1300 .0020 | 0.885 | 85.20 |

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TABLE 12 (Figure 21)

Experimental results for the hydrochlorination of Hevea latex at 2 Atm. total pressure, 1.95 Atm. HCl. and 69.5°C

| | | | | |
|---|---|---|---|---|
| 9P.1. | 30m | 0.9237. 0002 | 1.082 | 7.00 |
| 9P.2. | 61m | 0.9320 .0004 | 1.073 | 9.75 |
| 9P.3. | 95m | 0.9432 .0010 | 1.060 | 13.50 |
| 9P.4. | 120m | 0.9508 .0004 | 1.052 | 16.00 |
| 9P.5. | 138m | 0.9589 .0006 | 1.043 | 18.80 |
| 9P.6. | 155m | 0.9680 .0010 | 1.033 | 21.75 |
| 9P.7. | 180m | 0.9774 .0004 | 1.024 | 25.25 |
| 9P.8. | 210m | 0.9950 .0003 | 1.005 | 33.00 |
| 9P.9. | 240m | 1.0137 .0008 | 0.987 | 40.80 |
| 9P.10. | 300m | 1.0561 .0002 | 0.947 | 58.25 |
| 9P.11. | 330m | 1.0756 .0004 | 0.929 | 66.00 |
| 9P.12. | 420m | 1.1226. 0008 | 0.891 | 82.80 |
| 9P.13. | 370m | 1.1053 .0010 | 0.905 | 76.50 |
| 9P.14. | 600m | 1.1489 .0002 | 0.870 | 91.50 |

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TABLE 13 (Figure 21)

Experimental results for the Hydrochlorination of the fine fraction (F) of Hevea latex ($V_{o=}$.1.101) at 1.95 Atm of HCl and 69.5°C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 10P.1. | 35m | 0.9597±.0008 | 1.042 | 18.00 |
| 10P.2. | 40m | 0.9734 .0006 | 1.028 | 22.50 |
| 10P.3. | 55m | 0.9698 .0010 | 1.031 | 21.50 |
| 10P.4. | 1hr | 0.9682 .0010 | 1.033 | 21.00 |
| 10P.5. | 1hr 10m | 0.9852 .0005 | 1.015 | 27.75 |
| 10P.6. | 1hr 30m | 0.9776 .0002 | 1.023 | 24.50 |
| 10P.7. | 1hr 30m | 0.9983 .0008 | 1.002 | 33.25 |
| 10P.8. | 1hr 40m | 1.0080 .0015 | 0.993 | 37.25 |
| 10P.9. | 2hr | 0.9913 .0005 | 1.009 | 30.50 |
| 10P.10. | 2hr 10m | 1.0144 .0006 | 0.986 | 40.25 |
| 10P.11. | 2hr 20m | 1.0112 .0010 | 0.990 | 38.50 |
| 10P.12. | 2hr 40m | 1.0265 .0002 | 0.974 | 45.50 |
| 10P.13 | 3hr 5m | 1.0285 .0020 | 0.972 | 46.50 |
| 10P.14. | 3hr 30m | 1.0506 .0020 | 0.952 | 55.25 |
| 10P.15. | 4hr | 1.0687 .0010 | 0.935 | 62.50 |
| 10P.16. | 4hr 30m | 1.0868 .0010 | 0.919 | 70.00 |
| 10P.17. | 6hr | 1.1327 .0006 | 0.883 | 85.51 |

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TABLE 14 (Figure 21)

Experimental results for the hydrochlorination of the coarse fraction (C) of Hevea latex ($V_{o=}$.1.108) at 1.95 Atm of HCl and 69.5°C.

| | | | | |
|---|---|---|---|---|
| 11P.1. | 40m | 0.9214 .0002 | 1.086 | 6.30 |
| 11P.2. | 1hr | 0.9277 .0005 | 1.078 | 8.50 |
| 11P.3. | 1hr 30m | 0.9354 .0002 | 1.070 | 11.00 |
| 11P.4. | 1hr 40m | 0.9410 .0004 | 1.063 | 12.75 |
| 11P.5. | 2hr 20m | 0.9566 .0006 | 1.045 | 18.75 |
| 11P.6. | 3hr | 0.9690 .0005 | 1.032 | 22.75 |
| 11P.7. | 3hr 30m | 0.9972 .0002 | 1.003 | 34.50 |
| 11P.8. | 4hr | 1.0042 .0005 | 0.996 | 37.50 |
| 11P.9. | 4hr 30m | 1.0176 .0002 | 0.982 | 43.50 |

Table 22 (Figure 26)

Experimental results for the hydrochlorination of synthetic latex III ($V_o$=1.109) at 1.95Atm. HCl and 26.7°C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole% Reaction |
|---|---|---|---|---|
| LS.1. | 5m | 0.9526±.0008 | 1.049 | 19.06 |
| 1S.2. | 10m | 0.9634 .0010 | 1.038 | 22.97 |
| 1S.3. | 21m | 0.9841 .0002 | 1.016 | 31.34 |
| 1S.4. | 30m | 1.0002 .0008 | 1.000 | 37.78 |
| 1S.5. | 40m | 1.0180 .0004 | 0.983 | 45.10 |
| 1S.6. | 45m | 1.0286 .0005 | 0.972 | 50.10 |
| 1S.7. | 60m | 1.0674 .0020 | 0.937 | 67.50 |
| 1S.8. | 90m | 1.0968 .0008 | 0.911 | 85.92 |
| 1S.9. | 120m | 1.1082 .0010 | 0.903 | 95.20 |

Latex III made alkaline with 0.06% ammonia and left open to atmosphere for 4 days, $V_o$=1.097. This oxidized latex then reacted under above conditions . (Fig.27).

| | | | | |
|---|---|---|---|---|
| 1S10. | 10m | 0.9859 .0005 | 1.014 | 27.40 |
| 1S.11. | 20m | 1.0350 .0006 | 0.966 | 47.34 |
| 1S.12. | 30m | 1.0708 .0010 | 0.934 | 62.66 |

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Table 23 (Figure 26)

Experimental results for the hydrochlorination of synthetic latex III (Vo=1.109) at 1.95Atm.HCl and 69.5°C

| | | | | |
|---|---|---|---|---|
| 2S.1. | 2.5m | 0.9407 .0005 | 1.063 | 14.28 |
| 2S.2. | 5m | 0.9488 .0006 | 1.054 | 17.33 |
| 2S.3. | 11m | 0.9537 .0010 | 1.048 | 19.40 |
| 2S.4. | 15m | 0.9578 .0006 | 1.044 | 20.83 |
| 2S.5. | 20m | 0.9619 .0010 | 1.040 | 22.25 |
| 2S.6. | 30m | 0.9661 .0008 | 1.035 | 24.00 |
| 2S.7. | 60m | 0.9824 .0010 | 1.018 | 30.50 |
| 2S.8. | 90m | 0.9965 .0010 | 1.004 | 36.13 |
| 2S.9. | 180m | 1.0450 .0006 | 0.957 | 57.22 |

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Table 24 (figure 26)

Experimental results for the hydrochlorination of synthetic latex III ($V_o$=1.109) at 0.91 Atm. of HCl and 69.5° C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 3S.1. | 5m | 0.9367±.0002 | 1.067 | 12.94 |
| 3S.2. | 10m | 0.9444 .0008 | 1.059 | 15.63 |
| 3S.3. | 15m | 0.9484 .0006 | 1.055 | 16.98 |
| 3S.4. | 20m | 0.9510 .0026 | 1.052 | 18.19 |
| 3S.5. | 60m | 0.9593 .0006 | 1.043 | 21.18 |
| 3S.6. | 90m | 0.9629 .0015 | 1.039 | 22.62 |
| 3S.7. | 120m | 0.9654 .0010 | 1.036 | 23.72 |

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Table 25 (figure 26)

Experimental results for the hydrochlorination of Synthetic latex V ($V_o$=1.107) at 2Atm.ofHCl and 26.7°C.

| | | | | |
|---|---|---|---|---|
| 4S.1. | 5m | 0.9690 .0002 | 1.032 | 24.40 |
| 4S.2. | 9m | 0.9844 .0005 | 1.016 | 30.50 |
| 4S.3. | 20m | 1.0080 .0002 | 0.993 | 40.00 |
| 4S.4. | 30m | 1.0350 . 0002 | 0.9664 | 51.75 |
| 4S.5. | 41m | 1.0590 .0005 | 0.944 | 62.50 |
| 4S.6. | 50m | 1.0748 .0002 | 0.930 | 70.00 |
| 4S.7. | 110m | 1.1092 .0010 | 0.902 | 96.00 |

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Table 28 (figure 29)

Experimental results for the surface hydrochlorination of synthetic latex LII at 0.08 Atm. of HCl and 26.7°C ($V_o$=1.109)

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 5S.1. | 5m | 0.9074±.0006 | 1.102 | 2.04 |
| 5S.2. | 10m | 0.9117 .0010 | 1.097 | 3.53 |
| 5S.3. | 15m | 0.9128 .0008 | 1.095 | 4.10 |
| 5S.4. | 20m | 0.9132 .0008 | 1.095 | 4.10 |
| 5S.5. | 30m | 0.9130 .0020 | 1.095 | 4.10 |
| 5S.6. | 45m | 0.9159 .0002 | 1.092 | 5.03 |
| 5S.7. | 65m | 0.9163 .0004 | 1.092 | 5.03 |
| 5S.8. | 160m | 0.9220 .0005 | 1.085 | 7.18 |
| 5S.9. | 270m | 0.9240 .0010 | 1.082 | 8.13 |

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Table 29 (figure 29)

Experimental results for the surface hydrochlorination of synthetic latex III at 0.33 Atm. of HCl and 26.7°C ($V_o$=1.109)

| | | | | |
|---|---|---|---|---|
| 6S.1. | 5m | 0.9198 .0008 | 1.087 | 6.56 |
| 6S.2. | 8.5m | 0.9230 .0005 | 1.083 | 7.81 |
| 6S.3. | 10m | 0.9213 .0002 | 1.086 | 6.87 |
| 6S.4. | 12.5m | 0.9245 .0004 | 1.081 | 8.44 |
| 6S.5. | 15m | 0.9288 .0005 | 1.077 | 9.70 |
| 6S.6. | 17.5m | 0.9276 .0005 | 1.076 | 10.02 |
| 6S.7. | 20m | 0.9286 .0006 | 1.077 | 9.70 |
| 6S.8. | 25m | 0.9299 .0002 | 1.075 | 10.35 |
| 6S.9. | 50m | 0.9373 .0005 | 1.067 | 12.94 |
| 6S.10. | 40m | 0.9333 .0010 | 1.072 | 11.30 |
| 6s.11. | 60m | 0.9363 .0005 | 1.068 | 12.62 |
| 6S.12. | 90m | 0.9428 .0008 | 1.061 | 14.95 |
| 6S.13. | 150m | 0.9467 .0004 | 1.056 | 16.64 |
| 6S.14. | 270m | 0.9516 .0005 | 1.051 | 18.37 |

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Table 30 (figures 30 and 31)

Experimental results for the surface hydrochlorination of synthetic latex V ($V_o$=1.107) at 0.33 Atm. of HCl and 26.7°C. T=Reaction Duration, M=Mole.% Reaction and columns 2 and 6 used for the kinetic check plotted in figure 31.

| Sample | T | Density (d) | Specific Vol. (v) | M | Mx15/22 |
|---|---|---|---|---|---|
| 7S.1. | 4m | 0.9284±.0004 | 1.078 | 8.75 | 5.97 |
| 7S.2. | 8m | 0.9366 .0004 | 1.067 | 12.25 | 8.35 |
| 7S.3. | 10m | 0.9440 .0020 | 1.059 | 14.95 | 10.20 |
| 7S.4. | 12m | 0.9398 .0004 | 1.064 | 13.30 | 9.08 |
| 7S.5. | 20m | 0.9436 .0004 | 1.059 | 14.95 | 10.20 |
| 7S.6. | 27m | 0.9459 .0002 | 1.057 | 15.60 | 10.60 |
| 7S.7. | 23m | 0.9454 .0004 | 1.058 | 15.30 | 10.38 |
| 7S.8. | 35m | 0.9518 .0020 | 1.051 | 17.70 | 12.07 |
| 7S.9. | 47m | 0.9554 .0010 | 1.047 | 19.05 | 13.00 |
| 7S.10. | 90m | 0.9630 .0010 | 1.038 | 22.26 | 15.18 |
| 7S.11. | 122m | 0.9684 .0004 | 1.033 | 24.10 | 16.45 |
| 7S.12. | 240m | 0.9739 .0005 | 1.027 | 26.30 | 17.94 |

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Table 31 ( figures 30 and 31)

Experimental results for the surface hydrochlorination of synthetic latex V ($V_o$=1.107) at 0.22 Atm. of HCl and 26.7°C. Columns 6 and 7 used for the kinetic check plotted in figure 31.

| Sample | T | Density (d) | Spec. Vol.(V) | M | Mx15/22 | Tx0.45 |
|---|---|---|---|---|---|---|
| 8S.1. | 5m | 0.9174 .0002 | 1.091 | 4.75 | 3.24 | 2.25 |
| 8S.2. | 6m | 0.9288 .0002 | 1.077 | 9.10 | 6.21 | 2.70 |
| 8S.3. | 12m | 0.9286 .0005 | 1.077 | 9.10 | 6.21 | 5.40 |
| 8S.4. | 20m | 0.9360 .0005 | 1.068 | 11.95 | 8.15 | 9.00 |
| 8S.5. | 32m | 0.9398 .0006 | 1.064 | 13.30 | 9.07 | 14.40 |
| 8S.6. | 45m | 0.9431 .0002 | 1.060 | 14.60 | 9.96 | 2025 |
| 8S.7. | 62m | 0.9488 .0005 | 1.054 | 16.60 | 11.32 | 27.90 |
| 8S.8. | 80m | 0.9524 .0003 | 1.050 | 18.00 | 12.28 | 36.00 |
| 8S.9. | 105m | 0.9542 .0004 | 1.048 | 18.70 | 12.75 | 47.70 |
| 8S.10. | 240m | 0.9641 .0004 | 1.037 | 22.60 | 15.42 | 108.00 |

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Table 32 (figure 30)

Experimental results for the surface hydrochlorination of synthetic latex V ($V_o$=1.104) at 0.22 Atm. of HCl and 69.5°C.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 9S.1. | 5.5m | 0.9236±.0004 | 1.082 | 6.60 |
| 9S.2. | 10.5m | 0.9290 .0005 | 1.076 | 8.40 |
| 9S.3. | 21m | 0.9391 .0008 | 1.065 | 11.95 |
| 9S.4. | 27m | 0.9405 .0010 | 1.063 | 12.62 |
| 9S.5. | 31m | 0.9438 .0002 | 1.059 | 13.95 |
| 9S.6. | 45m | 0.9490 .0005 | 1.054 | 15.60 |
| 9S.7. | 61.5m | 0.9544 .0003 | 1.048 | 17.70 |
| 9S.8. | 90.5m | 0.9608 .0006 | 1.041 | 20.10 |
| 9S.9. | 121m | 0.9646 .0004 | 1.036 | 21.90 |
| 9S.10. | 151.5m | 0.9694 .0010 | 1.032 | 23.30 |
| 9S.11. | 180m | 0.9673 .0010 | 1.034 | 22.62 |
| 9S.12. | 209.5m | 0.9700.0010 | 1.031 | 23.68 |

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Table 33 (figure 32)

Experimental results for the hydrochlorination of vulcanized synthetic latex Va at 2Atm. HCl and 26.7°C.

| | | | | |
|---|---|---|---|---|
| 1V.1. | 3m | 0.9673 .0002 | 1.034 | 17.70 |
| 1V.2. | 6m | 0.9719 .0005 | 1.029 | 19.60 |
| 1V.3. | 10m | 0.9960 .0020 | 1.004 | 28.60 |
| 1V.4. | 15m | 1.0110 .0006 | 0.989 | 34.50 |
| 1V.5. | 20m | 1.0175 .0002 | 0.982 | 36.94 |
| 1V.6. | 25m | 1.0360..0010 | 0.964 | 42.90 |
| 1V.7. | 30m | 1.0540 .0006 | 0.949 | 51.90 |
| 1V.8. | 46m | 1.0803 .0008 | 0.926 | 63.30 |
| 1V.9. | 56m | 1.1014 .0010 | 0.908 | 73.00 |

$V_o$=1.090 for vulcanized latex Va

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Table 34 (figure 32)

Experimental results for the hydrochlorination of vulcanized synthetic latex Vb at 2 Atm. HCl and 26.7°C. Samples 2V.1. to 2V.4. had $V_o$=1.090, 2V.5. and 2V.6. had $V_o$=1.070.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 2v.1. | 32m | 1.0255±.0002 | 0.975 | 40.30 |
| 2V.2. | 39.5m | 1.0462 .0010 | 0.956 | 48.70 |
| 2V.3. | 43m | 1.0532 .0003 | 0.950 | 51.40 |
| 2V.4. | 55m | 1.0727 .0004 | 0.932 | 60.20 |
| 2V.5. | 5m | 0.9735 .0005 | 1.027 | 13.28 |
| 2V.6. | 10m | 0.9900 .0004 | 1.010 | 19.05 |

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Table 35 (figure 29)

Experimental results for the surface hydrochlorination of vulcanized synthetic latex IIIa at 0.33 Atm. HCl and 26.7°C. $V_o$=1.099

| | | | | |
|---|---|---|---|---|
| 3V.1. | 7.5m | 0.9246 .0005 | 1.084 | 5.34 |
| 3V.2. | 18m | 0.9288 .0004 | 1.077 | 6.56 |
| 3V.3. | 29m | 0.9354 .0008 | 1.070 | 8.75 |
| 3V.4. | 55m | 0.9360 .0005 | 1.068 | 9.39 |
| 3V.5. | 80m | 0.9426 .0005 | 1.061 | 11.63 |
| 3V.6. | 120m | 0.9496 .0010 | 1.053 | 14.28 |
| 3V.7. | 270m | 0.9552 .0005 | 1.047 | 16.30 |

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Table 36 (figure 33)

Experimental results for the surface hydrochlorination of synthetic vulcanized latex Va at 0.33 Atm. HCl and 26.7°C. $V_o$=1.090.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole.% Reaction |
|---|---|---|---|---|
| 4V.1. | 7m | 0.9390±.0004 | 1.065 | 7.50 |
| 4V.2. | 15m | 0.9492 .0020 | 1.054 | 11.00 |
| 4V.3. | 25m | 0.9558 .0002 | 1.048 | 12.95 |
| 4V.4. | 35m | 0.9580 .0010 | 1.044 | 14.25 |
| 4V.5. | 51m | 0.9578 .0008 | 1.044 | 14.25 |
| 4V.6. | 60m | 0.9598 .0002 | 1.042 | 14.95 |
| 4V.7. | 95m | 0.9615 .0010 | 1.040 | 15.60 |
| 4V.8. | 120m | 0.9679 .0020 | 1.033 | 18.00 |
| 4V.9. | 230m | 0.9730 .0005 | 1.028 | 19.75 |

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Table 37 (figure 33)

Experimental results for the surface hydrochlorination of vulcanized synthetic latex Vb at 0.33 Atm. HCl and 26.7°C. $V_o$=1.081.

| Sample | Reaction Duration | Density (d) | Specific Volume (V) | Mole% Reaction |
|---|---|---|---|---|
| 5V.1. | 10m | 0.9409 .0010 | 1.063 | 5.30 |
| 5V.2. | 20m | 0.9460 .0002 | 1.057 | 7.20 |
| 5V.3. | 30m | 0.9495 .0002 | 1.053 | 8.40 |
| 5V.4. | 45m | 0.9536 .0002 | 1.048 | 10.00 |
| 5V.5. | 75m | 0.9596 .0006 | 1.042 | 11.95 |
| 5V.6. | 121m | 0.9633..0005 | 1.038 | 13.30 |
| 5V.7. | 240m | 0.9668 .0008 | 1.034 | 14.60 |

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## REFERENCES


(1) Bunn,C.W.,& Garner,E.V., J.Chem.Soc., p.654,(1942).
(2) Weber,C.O., Ber. 33, 789, (1900).
(3) Ind.Eng.Chem., (News Ed.), 12, 444,(1934).
(4) Gehmann,S.D., Field,J.E.,& Dinsmore,R.P., Proc.Rubber Tech.Conf., London,p.961,(1938).
(5) Rubber Age and Synthetics, p.79, (May,1947).
(6) Belgrave,W.N.C., Malayan Agr. J., 11, 348, (1923).
(7) Blow,C.M., Proc.Rubber Tech.Conf.,London,p.186,(1938).
(8) Hassels,J.H.E., Chem. Weekblad , 37, 467, (1940).
(9) van Veersen, G.J., (To Rubber Stichting), Brit.Patent Applic., 28,350/47, (1947).
(10) van Veersen,G.J., (To Rubber Stichting), Brit. Patent Applic. 15088/48, (1948).
(11) Gordon,M., (To Dunlop Rubber Co.), Brit.Patent Applic. 634,879, (1950).
(12) Gordon,M., Ind.Eng.Chem., 43, 386, (1951).
(13) Gordon,M.& Everett,R.M., (To Dunlop Rubber Co.), Brit. Patent, 647,752, (1950).
(14) van Amerongen,G.J., Ind.Eng.Che m., 43, 2535, (1951).
(15) D'Ianni,J.D.,Naples,F.J.,Marsh,J.W.,& Zarney,J.L., Ind.Eng.Chem.,38, 1178, (1946).
(16) D'Ianni,J.D., Ind.Eng.Chem., 40, 253, (1948).
(17) van Veersen,G.J., Proc.Rubber Tech.Conf.,London, p.87, (1948).
(18) Gordon,M.& Taylor,J.S., J.Appl.Chem., 2, 493, (1952).
(19) Yeck,R.P.& Kissin,H.G., Ind. Eng.Chem.,(Anal.Ed.), 17, 692, (1945).
(20) Boyer,R.F.,Spencer,R.S.,& Wiley,R.M., J.Polymer Sci., 1, 249, (1946).
(21) Berg,S., Kolloid-Beihefte , 5, 1, (1941).
(22) Gordon,M.& McNab,I.A., Trans.Faraday Soc.,49,31,(1953).
(23) de Vries,O., India Rubber J., p.9, (March, 1935).
(24) Rhodes,E., India Rubber J., p.7, (April, 1935).
25 ) McPherson,R., Bur.Stand.J.Res., 8, 751, (1932).
(26) Taylor,D:, J.Chem.Soc., p.232, (1951).
(27) Libman,D.D., Chem.&Ind., 67, 728, (1948).
(28) Hammett,L.P.,"Physical Organic Chemistry", pp.233,311, N.Y. McGraw Hill, (1940).
(29) Harned,H.S.,& Seltz,H., J.Amer.Chem.Soc., 44,1475,(1922)
(30) van Veersen,G.J., Rec.Trav.Chim.Pays-Bas,69,1365,(1950)
(31) Gordon,M., Proc.Roy.Soc., A204, 569, (1951).
(32) Gordon,M., Disc.Faraday Soc.,10, 125, (1951).
(33) Grassie,N., Trans Faraday Soc., 48, 379, (1952).
(34) Bovey,D.M.,& Turner,E.E., J.Chem.Soc., p.3223, (1951).
(35) Thomson,F.W.,& Ubbelohde,A.R., Trans.Faraday Soc., 46,349(1950).

(36) Bastiansen,O.,& Hassel,O., Nature,London, 157, 765, (erratum,871),(1946).
(37) Bunn,C.W.,& Peiser,H.S., Nature,London, 159, 161,(1947).
(38) Bunn,C.W., Nature, London, 161, 929, (1948).
(39) Bunn,C.W., J.Appl.Chem., 1, 266, (1951).
(40) Meyer,K.H.,& Mark,H., Ber., 61, 1939, (1928).
(41) Gehmann,S.D., Chem.Rev., 26, 203, (1940).
(42) Bunn,C.W., Proc.Roy.Soc., A180, 40, (1942).
(43) Field,J.E.,Woodford,D.E.,& Gehmann,S.D., J.Appl.Phys.,17, 386, (1946).
(44) Williams,D.,& Dale,B., J.Appl.Phys.,15, 585, (1944).
(45) Thompson,H.W.,& Torkington,P.,Trans.Faraday Soc., 41, 246, (1945).
(46) Richardson,W.S.,& Sacher,A., J.Polymer Sci.,10,353, (1953).
(47) Hart,E.J.,& Meyer,A.W., J.Amer.CHem.Soc.,71,1980,(1949).
(48) Hughes,G.,Ingold,C.K.,& Reed,R.I., J.Chem.Soc., p.2410,(1950).
(49) Crampsey,E.,Gordon,M.,& Taylor,J.S., J.Chem.Soc., p.3925, (1953).
(50) U.S.Patent, 1,896,491 .
(51) Whitmore,F.C.,"Organic Chemistry",P.45, N.Y., D.Van Nostrand,(1937).
(52) Harries,C.,& Fonrobert,E., Ber., 46, 773, (1913).
(53) Van den Tempel,M., Trans.Inst.Rubber Ind.,27,290,(1951).
(54) Jellinek,H.H.G., J.Polymer Sci., 9, 369, (1952).
(55) Wynne Jones,W.F.K., J.Chem.Soc., p.1064, (1930).
(56) Scatchard,G., Chem.Rev.,10, 229, (1932).
(57) La Mer,V.K., J.Amer.Chem.Soc.,57, 2669,(1935).
(58) Fuoss,R.M.,& Kraus,C.A.,J.Amer.Chem.Soc.,55,2387,(1933).
(59) Plesch,P.H.,& Flett,M.St.C.,J.Chem.Soc.,p.3355,(1952).
(60) Overberg,C.G.,& Endres,G.F., 5th Canadian High Polymer Forum , (1953).
(61) Grün,F., Experientia, 3, 490, (1947).
(62) Hudson,R.F., Disc.Faraday Soc., 16, 14, (1954).
(63) Peters,L.,& Lester,G.H., Disc.Faraday Soc.,16,24,(1954).
(64) Gordon,M.,& Taylor,J.S., 3rd Rubber Tech.Conf., London, (1954),(in press).
(65) Gordon,M.,& Taylor,J.S.,J.Appl.Chem.,3, 537,(1953).

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